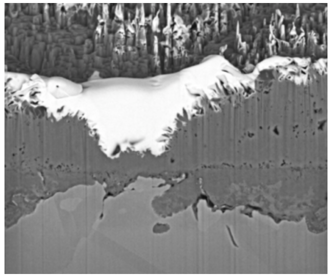
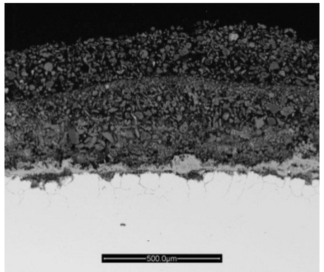
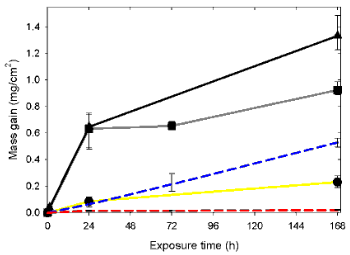
Critical corrosion phenomena during combustion of biomass and waste

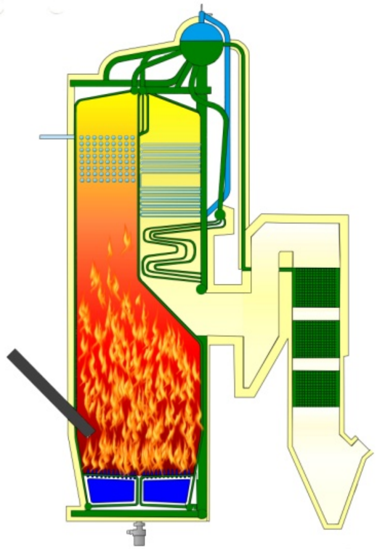
The
High-Temperature
Corrosion Center

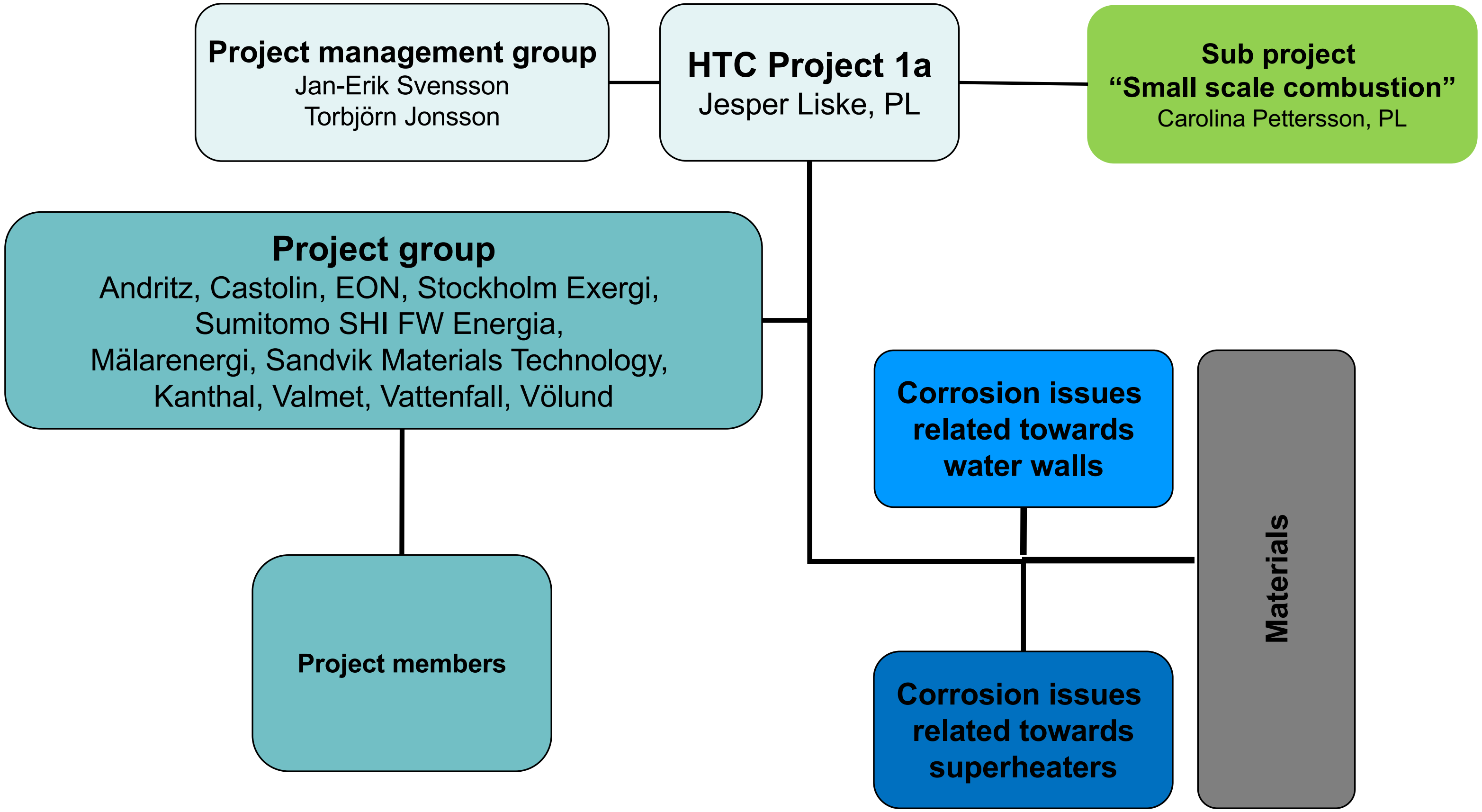
A. Persdotter, A. Olivas, A. Talus, B. Jönsson, E. Larsson, J-E. Svensson, J. Liske, J. Eklund, J. Photer, K. Hellström, L-G. Johansson, L. Paz, N. Israelsson, R. Norling, S. Bigdeli, S. Karlsson, T. Jonsson, V. Asokan










Project management group
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Corrosion issues related towards water walls
Materials
Project members
Corrosion issues related towards superheaters

Project aims (from the 4-year plan)

- The aim of this project is to **generate new knowledge** about high temperature corrosion by conducting research, to help solve a number of corrosion problems, which restrict the development of more energy efficient processes and technologies during combustion of biomass and waste. The research within this project is directed towards **superheater** and **water wall corrosion**, but could also be applied in other parts of the boiler (e.g. uncooled surfaces or economizer).
- The aim is to provide **guidance on measures to mitigate corrosion**, for example avoiding corrosion problems when deploying potentially corrosive fuels in plants. Such measures include **alteration of the flue gas chemistry**, **optimization of materials selection** and improved routines in boiler operation.

Research areas within HTC1a

Superheater corrosion

Water wall corrosion

Material research incl coatings (low alloyed steels, stainless steels, FeCrAl alloys)

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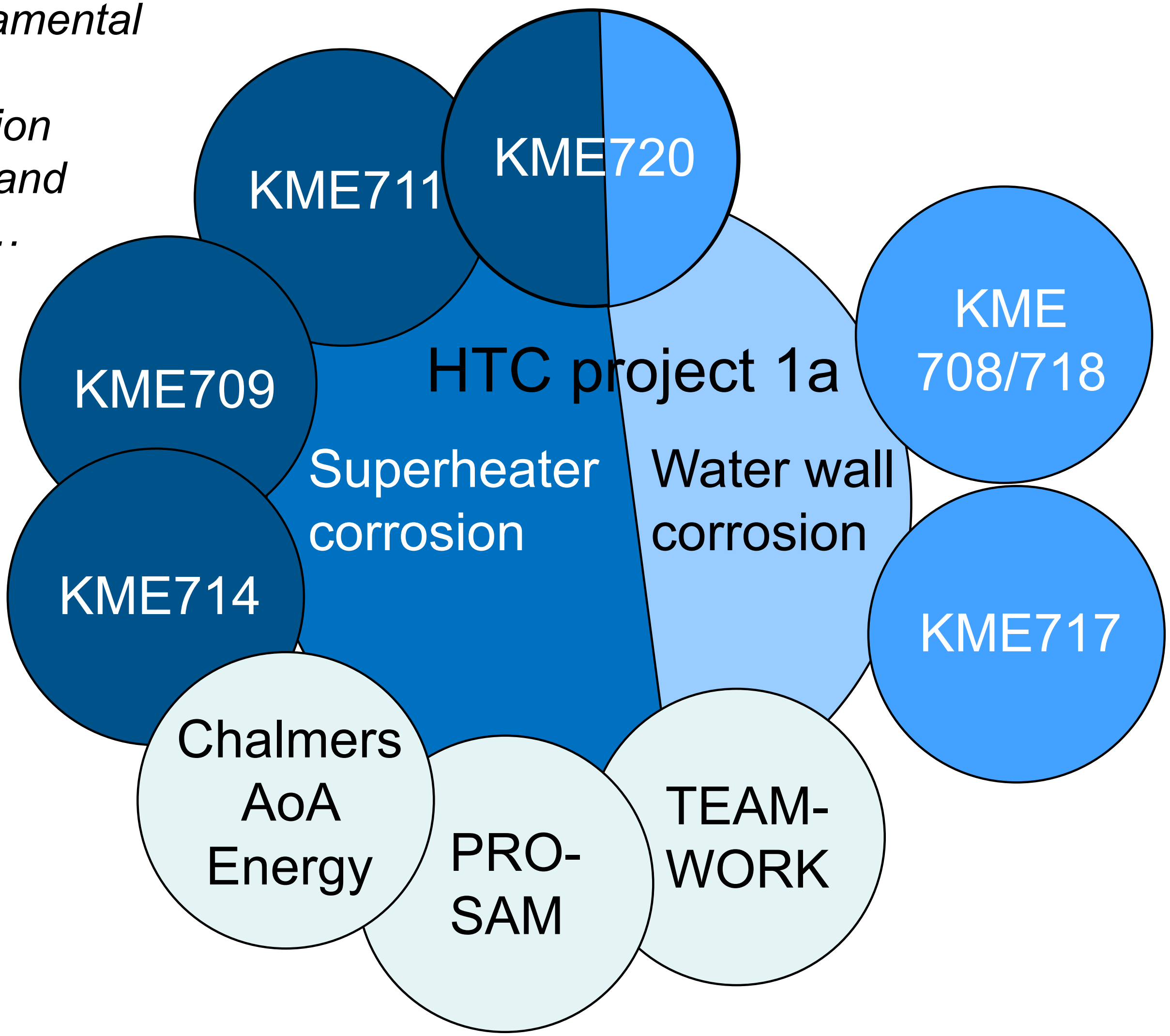
- The aim is to provide **guidance on measures to mitigate corrosion**, for example avoiding corrosion problems when deploying potentially corrosive fuels in plants. Such measures include **alteration of the flue gas chemistry**, **optimization of materials selection** and improved routines in boiler operation.

- This project will serve as a **platform for fundamental research of high temperature corrosion related to biomass and waste fired boilers.** The project will also be a forum for the member companies, the fundamental knowledge shared within the project aiding the companies in the development of new improved products and services.

- **The fundamental research conducted within this project is coupled to more field oriented projects (funded by e.g. KME**), which aims to reduce corrosion related maintenance and unplanned downtime and reducing the cost of new boilers through optimized material selection.

…platform for fundamental research of high temperature corrosion related to biomass and waste fired boilers…




Project objectives
4-year project plan
Project goals


Project objectives
4-year project plan
2014 project plan
2015 project plan
2016 project plan
2017 project plan
Project goals
Reporting, feedback and revised project plan

Research topics

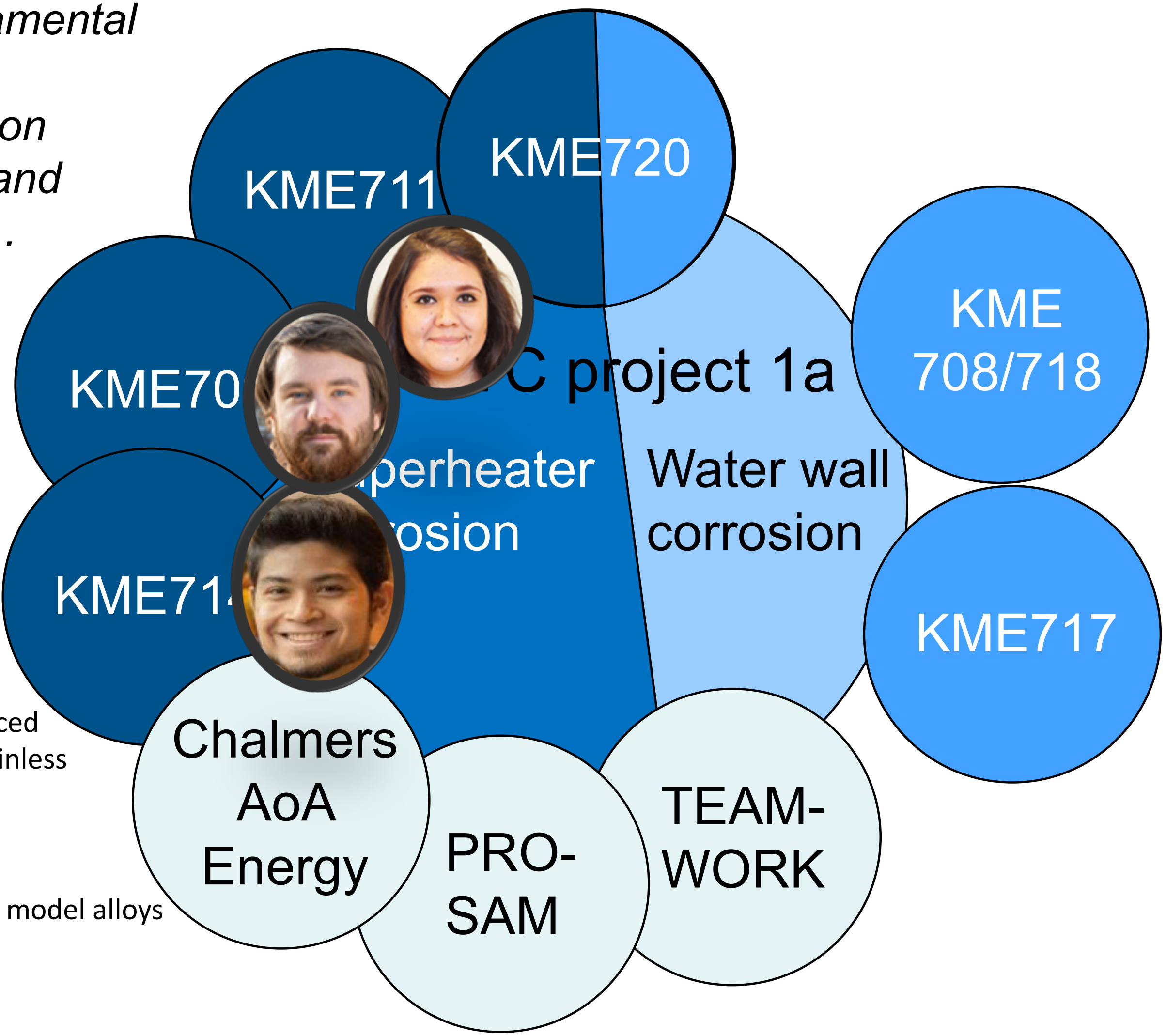
Superheater corrosion

- *Steady state oxidation with the formation of reaction zones*
- *The effect of corrosive deposits and gases on future corrosion resistance – Corrosion memory*
- *Influence of continuous addition of KCl*
- *A mechanistic study of chlorine induced corrosion*
- *Material research including model alloys focusing on superheater corrosion*

Waterwall corrosion

- *Melt induced corrosion?*
- *Investigate different materials and different heavy metal salts*
- *The effect of varying oxygen levels in the $PbCl_2$-induced corrosion*

…platform for fundamental research of high temperature corrosion related to biomass and waste fired boilers…



The effect of the amount of KCl on the mode of corrosion
Julien Phother, Chalmers

High temperature chlorine-induced corrosion of low-alloyed and stainless steel – The role of oxide scales
Andrea Olivas, Chalmers

The effect of Cr and Si on FeCrAl model alloys in KCl environments
Johan Eklund, Chalmers

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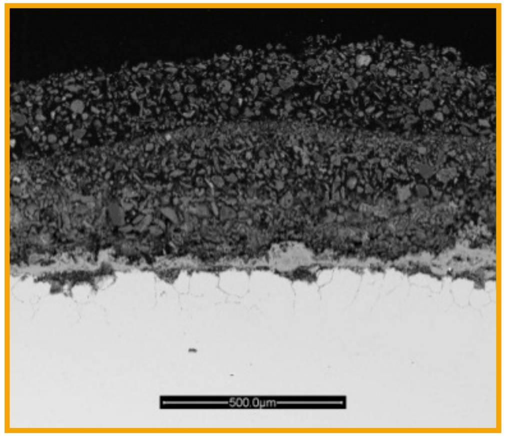
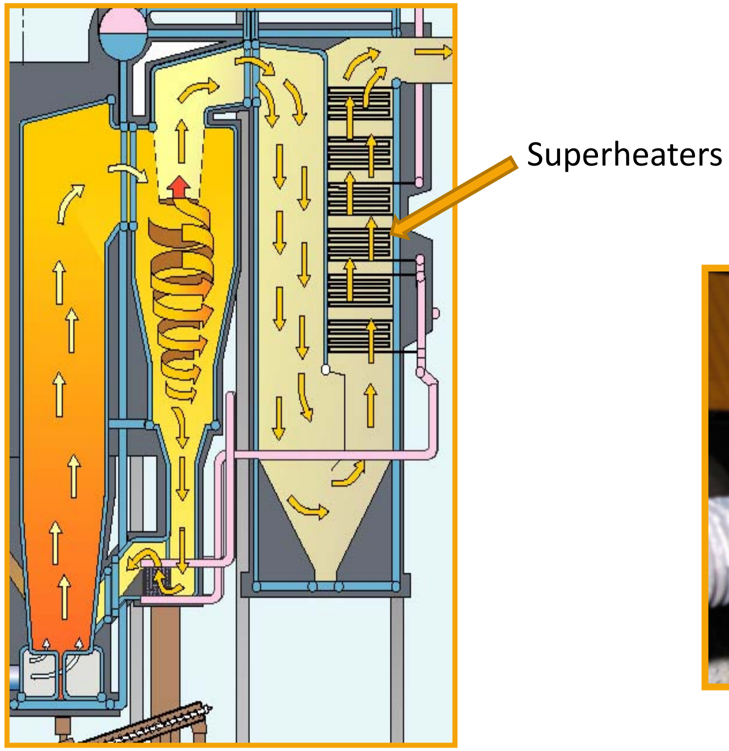
Challenging alloys in the lab
A way to mimic a boiler



Julien Phother

Boiler and corrosion



Deposits and corrosion

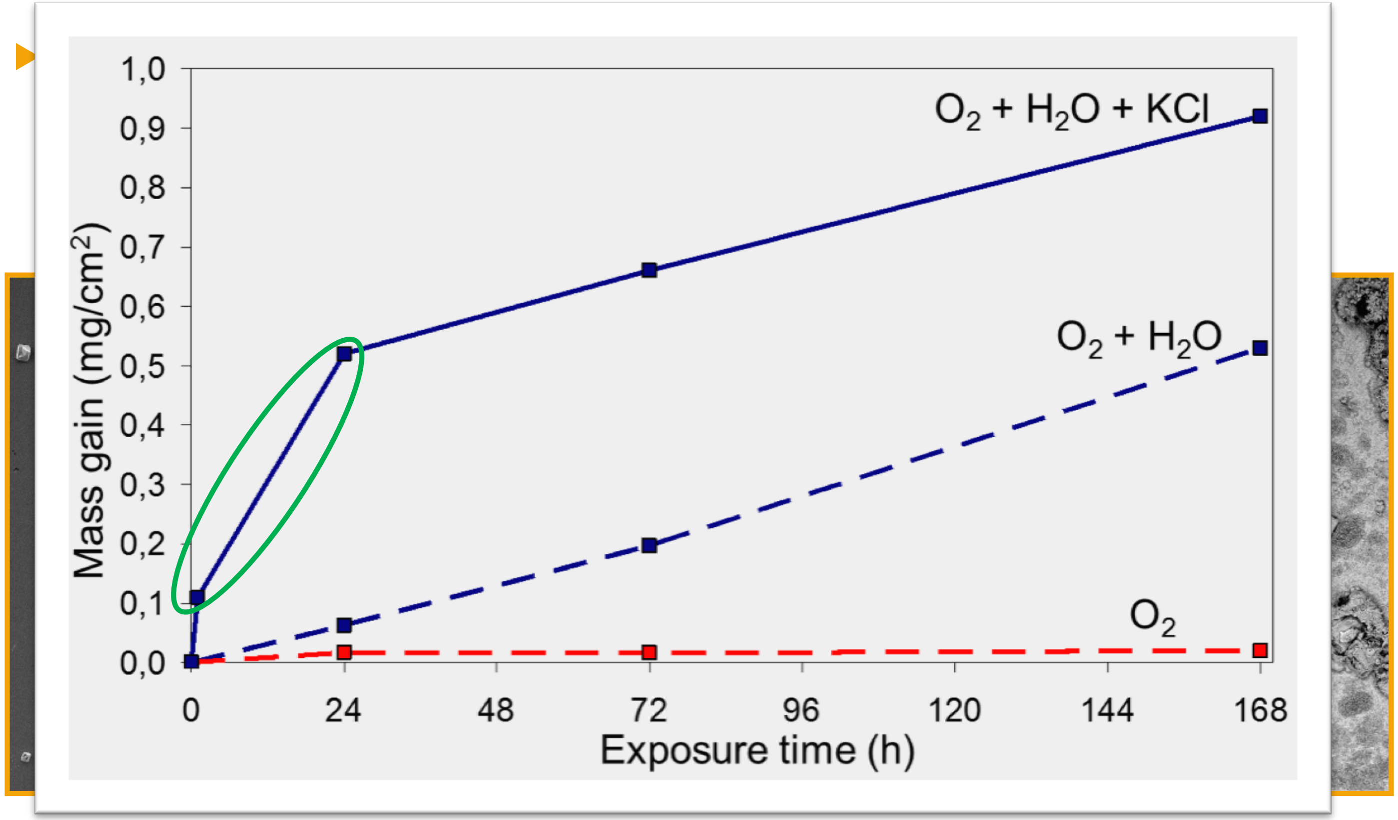
Substance	Fossil fuel	Biomass and waste
pO_2	~1%	~5%
pH_2O	~10%	20-30%
Release of alkali compounds	low	high
pSO_2	high	low
pHCl	high	low/high

- Corrosion resistance of stainless steels : Cr rich oxide film
- Depletion of Cr from the oxide :

$$(Cr,Fe)_2O_3 \xrightarrow{O_2 + H_2O(g)} Fe_2O_3 + CrO_2(OH)_2(g)$$

$$(Cr,Fe)_2O_3 \xrightarrow[O_2 + KCl]{} Fe_2O_3 + K_2CrO_4$$

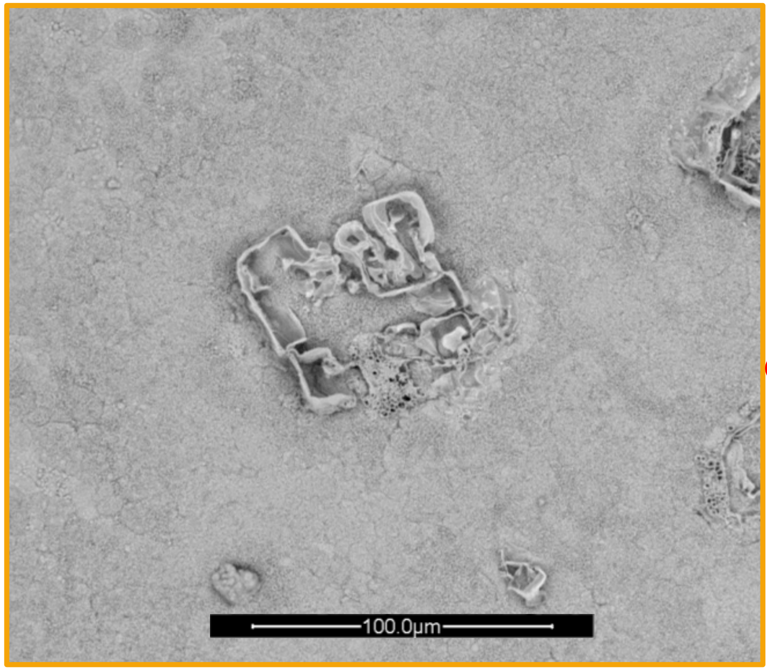
KCl lab exposures 304L

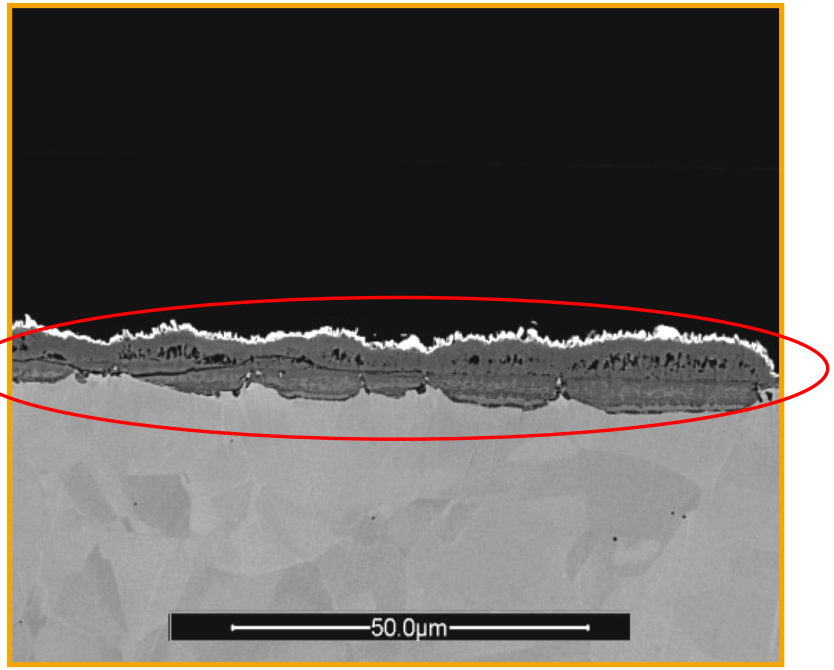


KCl lab exposures 304L

0,1 mg/cm²

Not severe corrosion



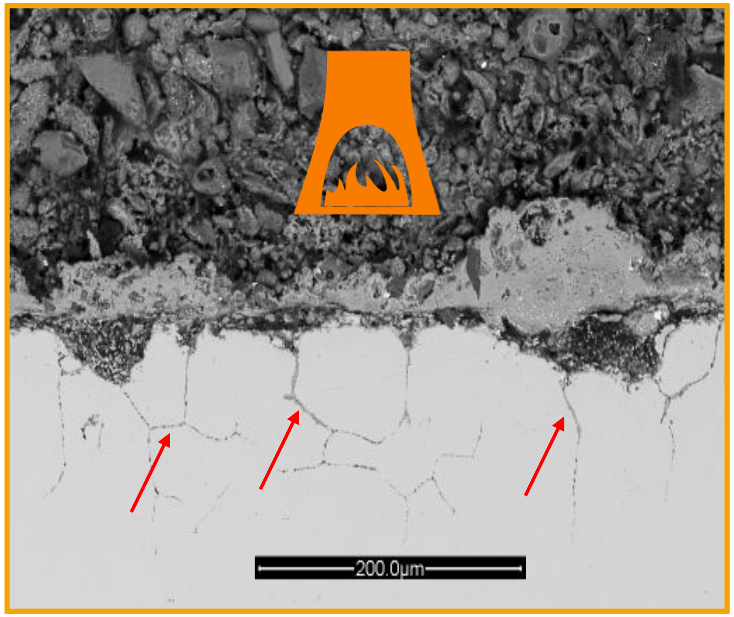


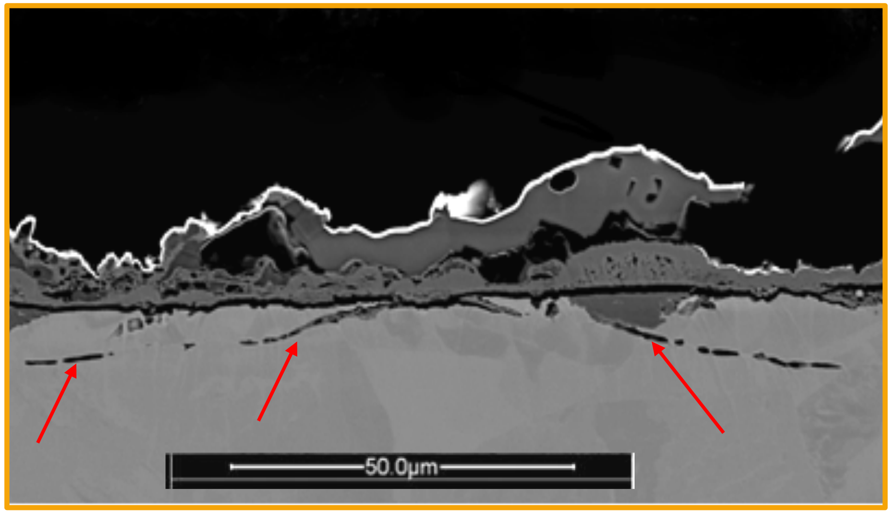
~ 10 µm

KCl lab exposures 304L

1,0 mg/cm²

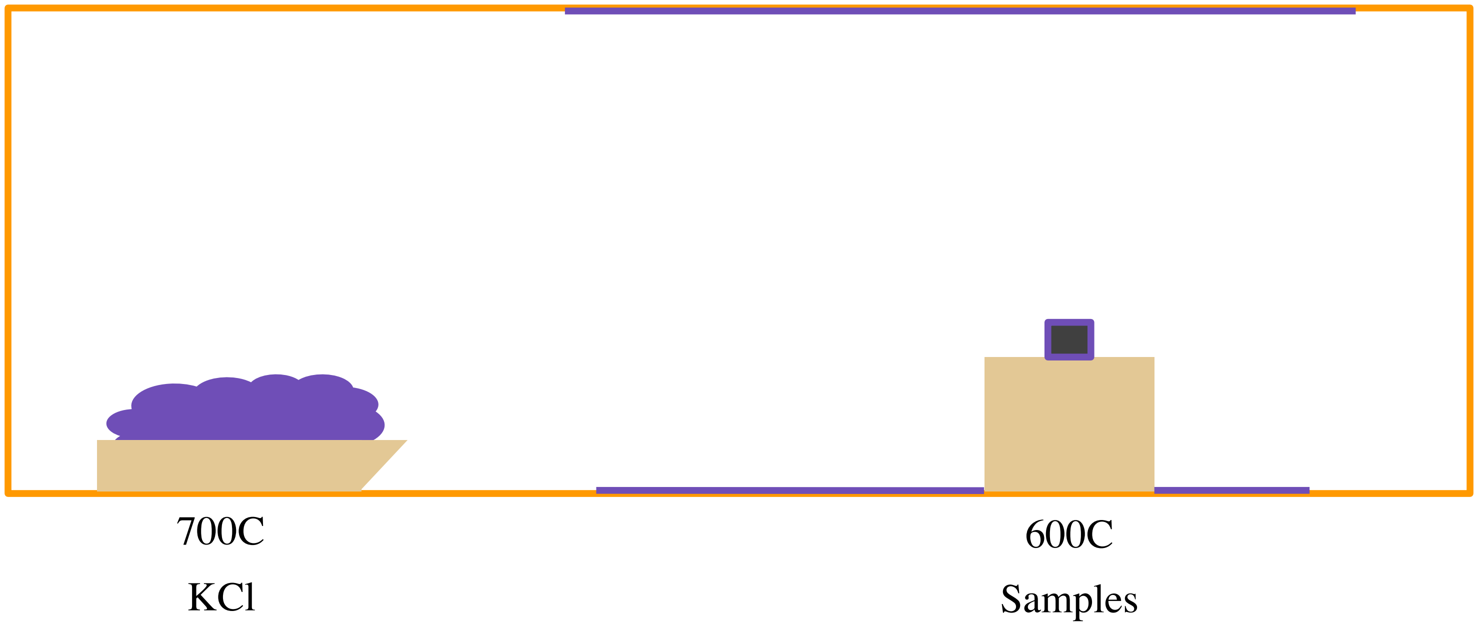
More severe corrosion





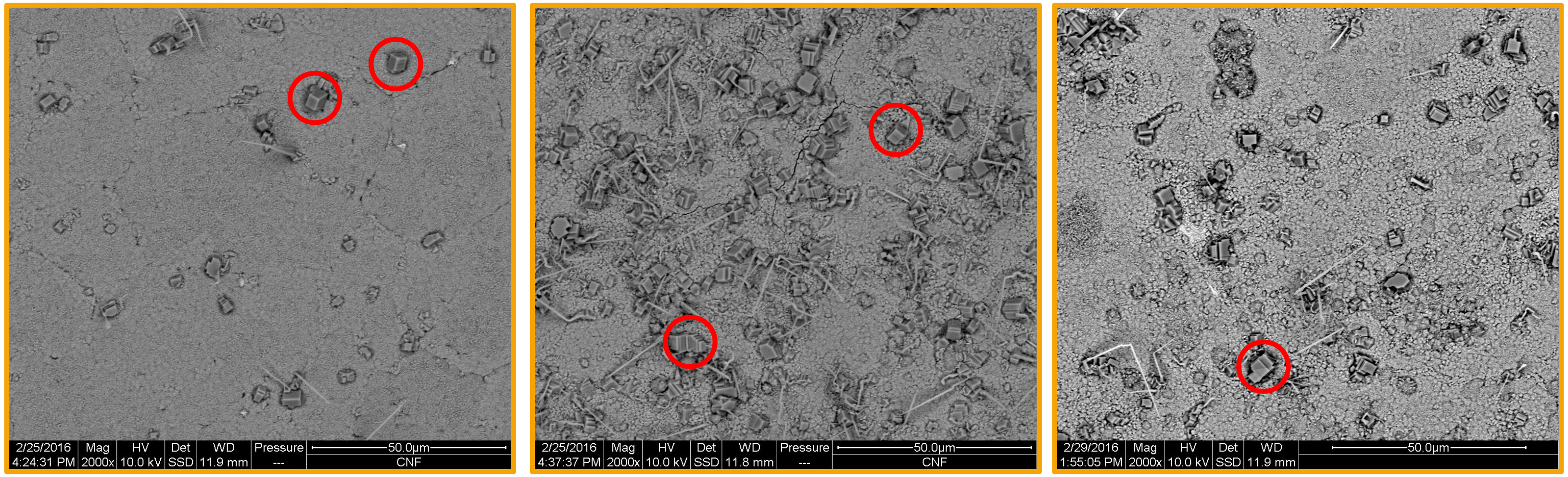
Next step :
KCl added continuously

KCl added continuously

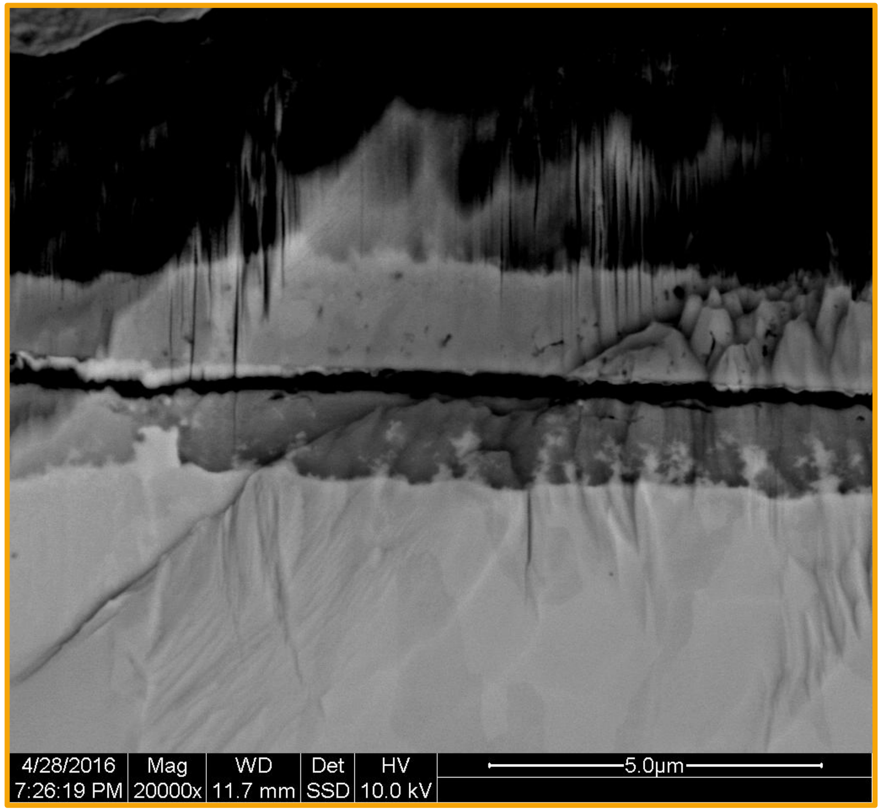


Experiment 304L

1H

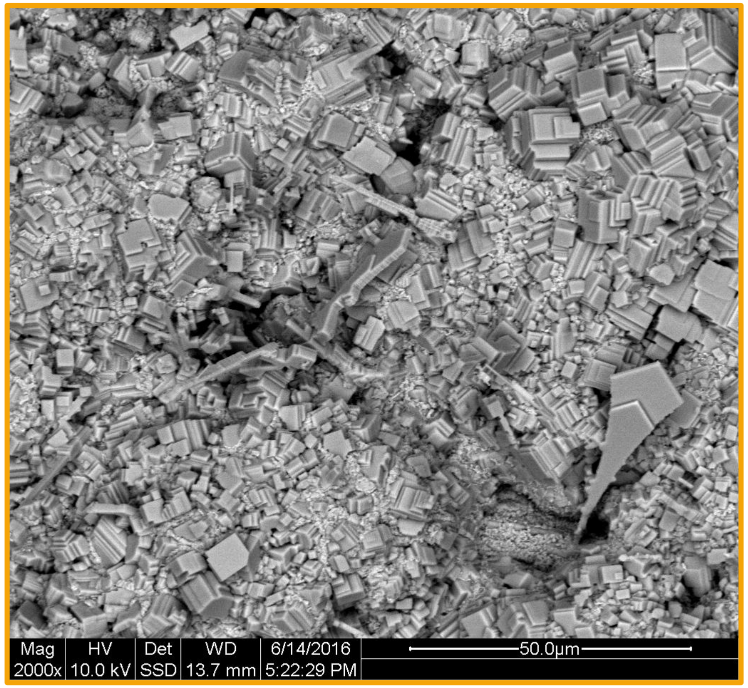


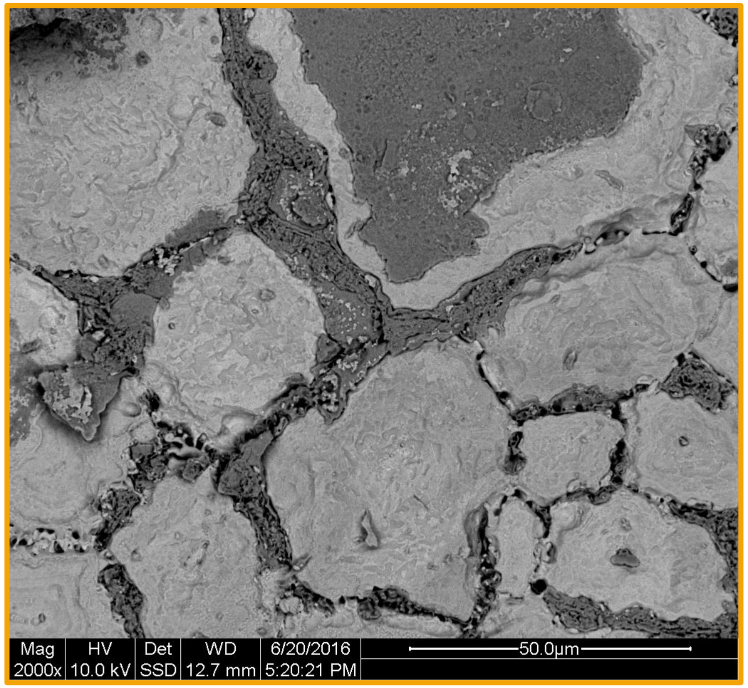
1H

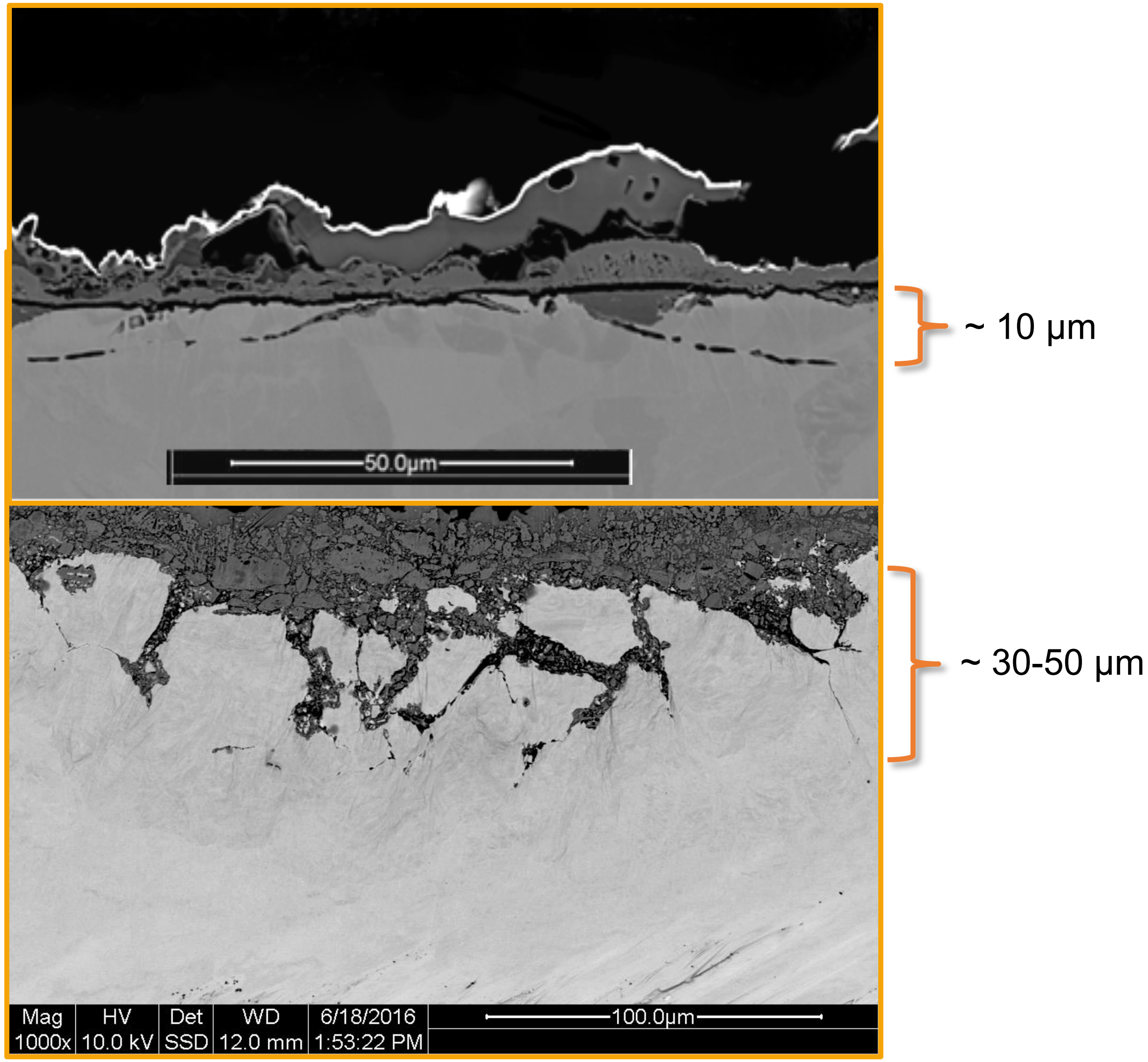

4/28/2016 7:26:19 PM
Mag 20000x
WD 11.7 mm
Det SSD
HV 10.0 kV
5.0µm
Fe_2O_3
$(Cr,Fe,Ni)_3O_4$
~ 2,9 µm

Experiment 304L

24H

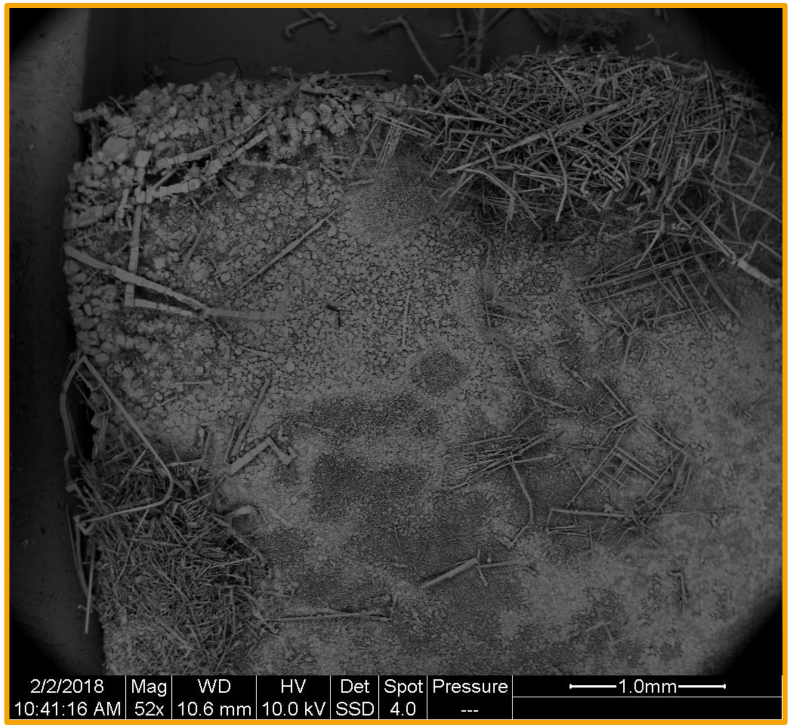


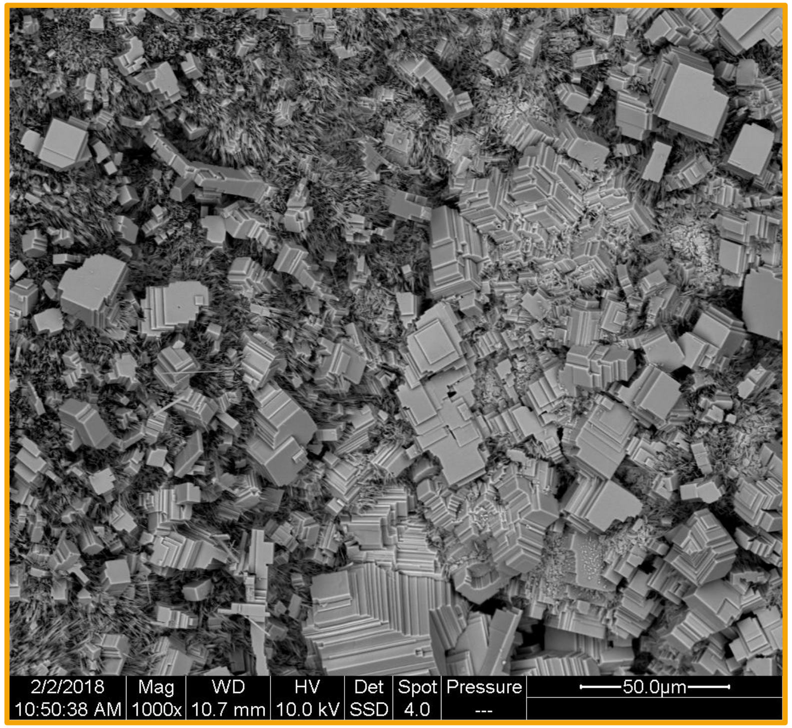



50.0µm
~ 10 µm
~ 30-50 µm
Mag
1000x
HV
10.0 kV
Det
SSD
WD
12.0 mm
6/18/2016
1:53:22 PM
100.0µm

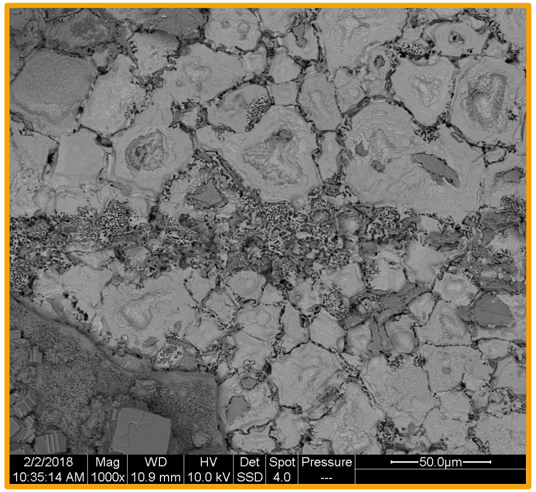
Experiment 304L

168H





168H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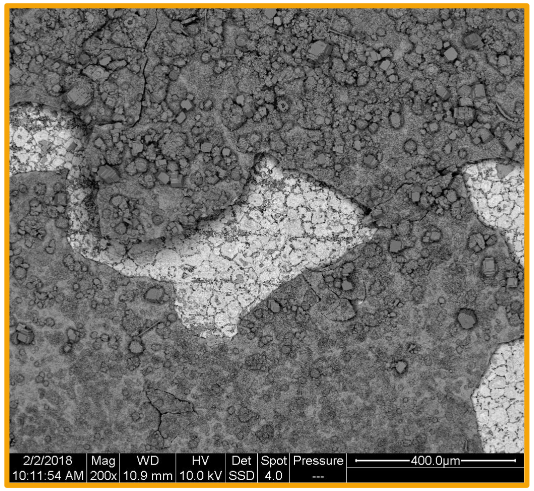
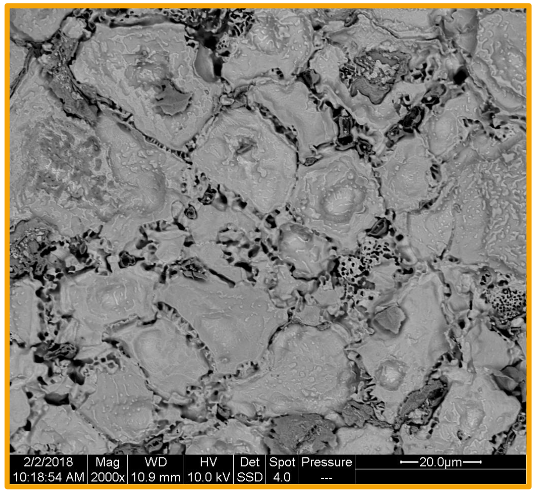

2/2/2018 10:11:54 AM | Mag 200x | WD 10.9 mm | HV 10.0 kV | Det SSD | Spot 4.0 | Pressure --- | 400.0µm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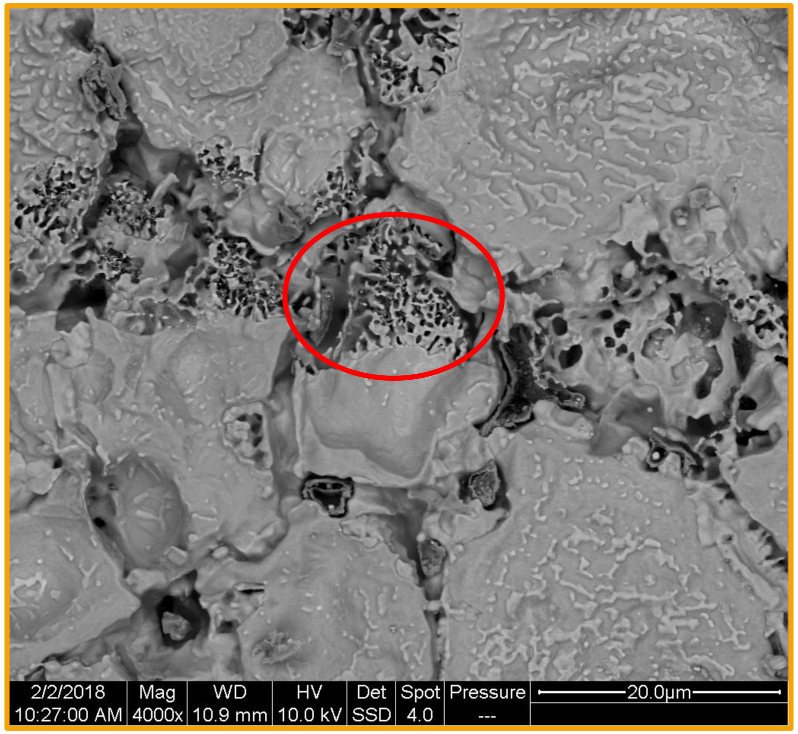
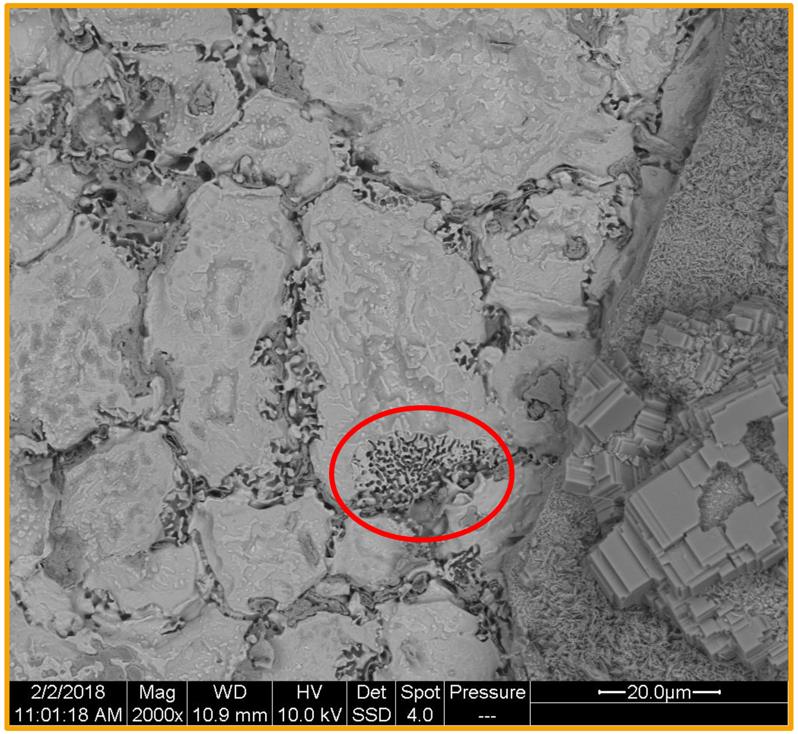
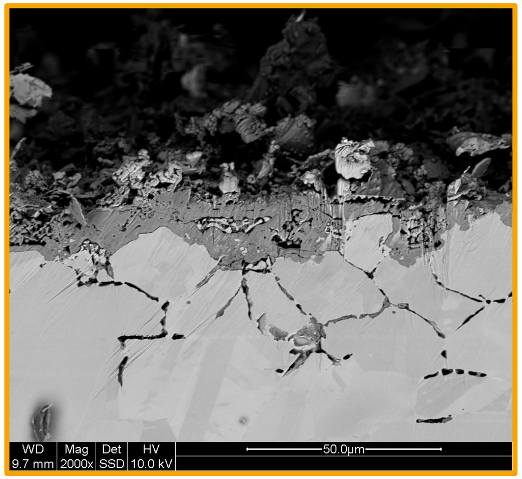
168H

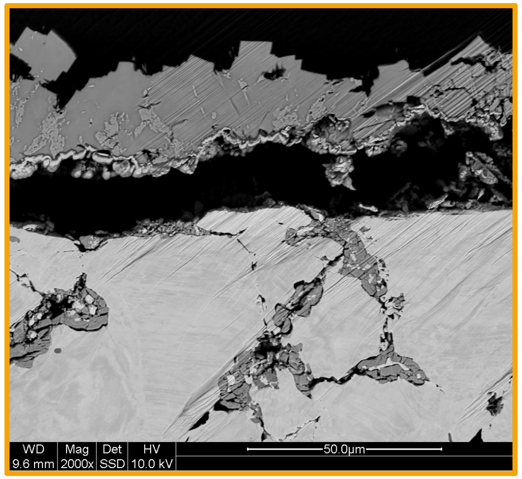

2/2/2018 10:27:00 AM
Mag 4000x
WD 10.9 mm
HV 10.0 kV
Det SSD
Spot 4.0
Pressure ---
20.0µm

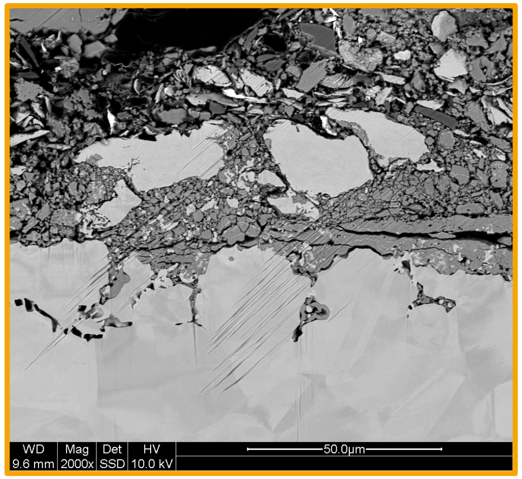

2/2/2018 11:01:18 AM
Mag 2000x
WD 10.9 mm
HV 10.0 kV
Det SSD
Spot 4.0
Pressure ---
20.0µm

168H

Grain boundary attack depth ~ 20-50 µm







Conclusions

~ 10 µm

~ 30 - 50 µm

~ 180 µm

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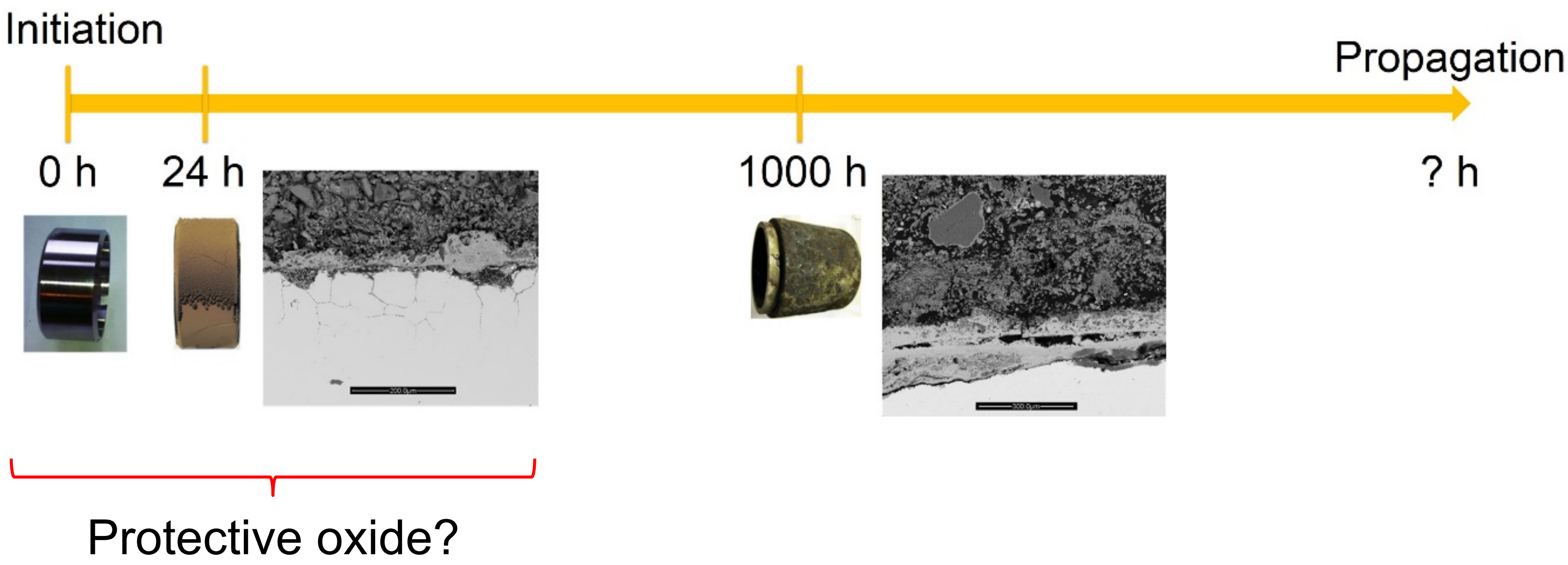
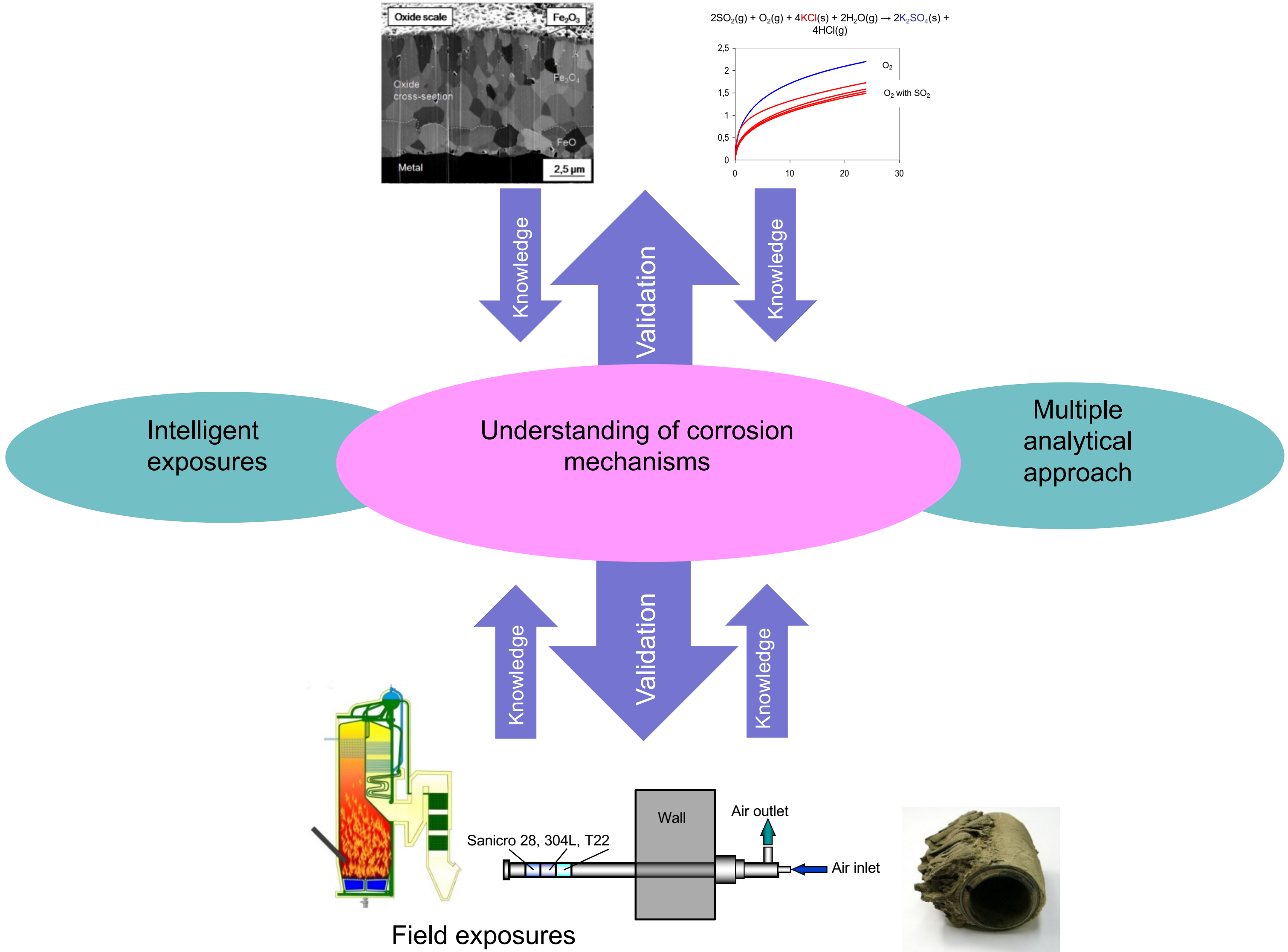
Mechanistic study of chlorine penetration of oxide scales

Andrea Olivas

How are different oxides affected by a corrosive environment?

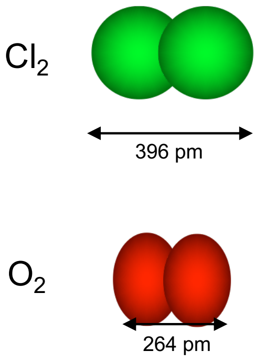


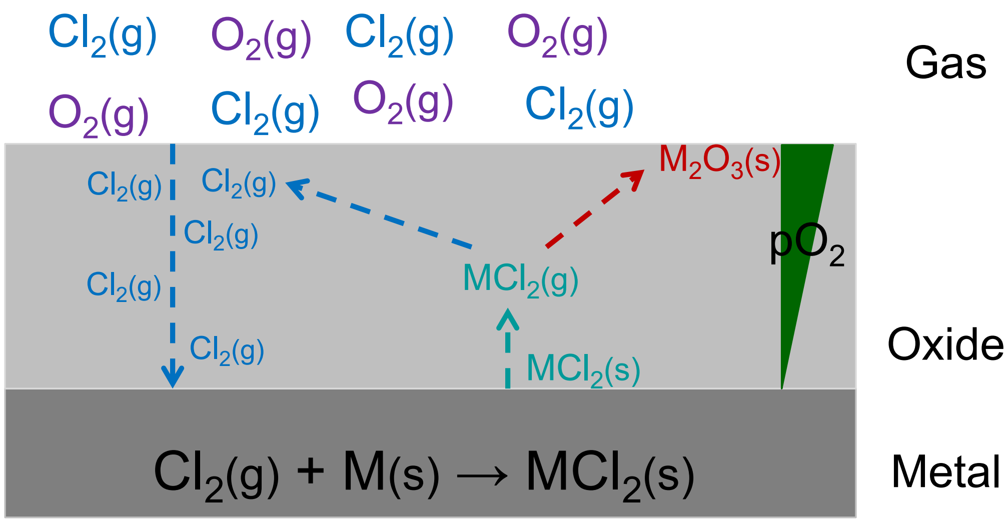

Oxide scale
Fe_2O_3
Oxide cross-section
Fe_3O_4
FeO
Metal
2,5 µm
$2SO_2(g) + O_2(g) + 4KCl(s) + 2H_2O(g) \rightarrow 2K_2SO_4(s) + 4HCl(g)$
O_2
O_2 with SO_2
Knowledge
Validation
Knowledge
Intelligent exposures
Understanding of corrosion mechanisms
Multiple analytical approach
Knowledge
Validation
Knowledge
Wall
Air outlet
Sanicro 28, 304L, T22
Air inlet
Field exposures

Influence of Chlorine

Active Oxidation – Chlorine Cycle

$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + Cl_2(g)$$





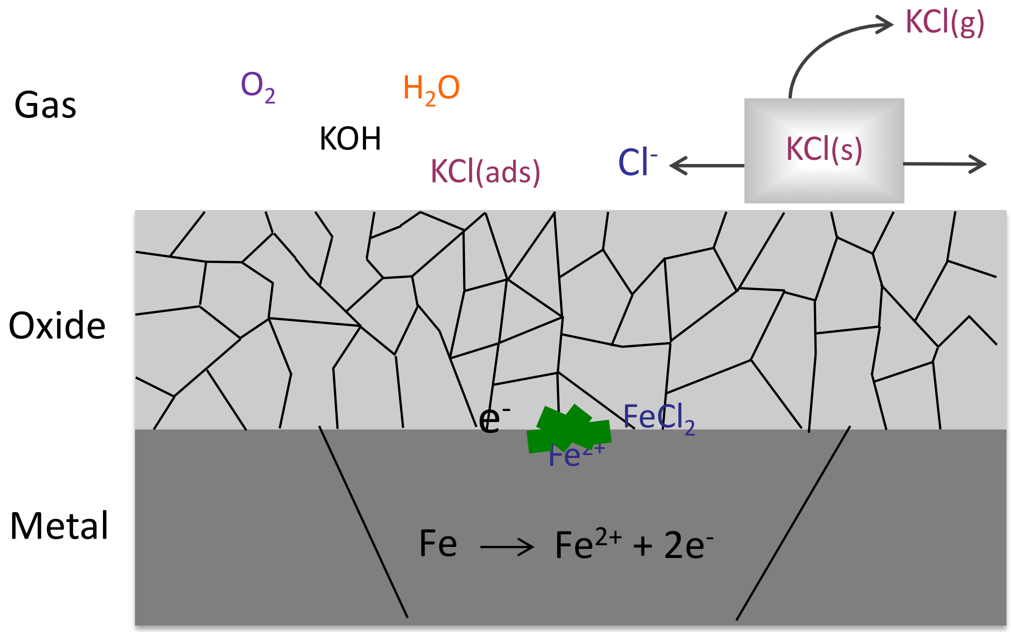
$$2MCl_2(g) + 1/2O_2(g) \rightarrow M_2O_3(s) + 2Cl_2(g)$$

Grabke, H.J., E. Reese, and M. Spiegel, *The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits.* Corrosion Science, 1995. **37**(7): p. 1023-1043.

Chlorine-induced corrosion

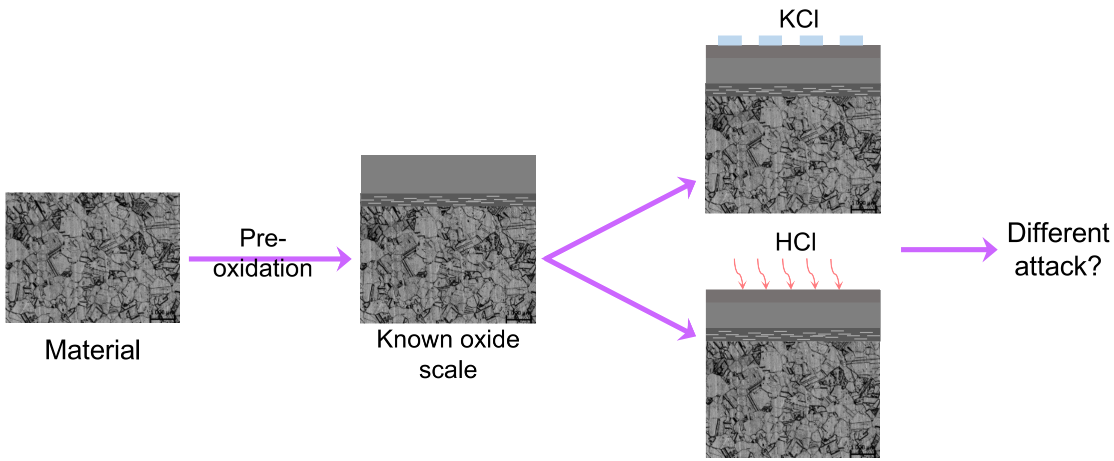
Scheme of KCl-induced corrosion

$$2KCl(ads) + 1/2O_2(g) + H_2O(g) + 2e^- \rightarrow 2KOH(g) + 2Cl^-(ads)$$

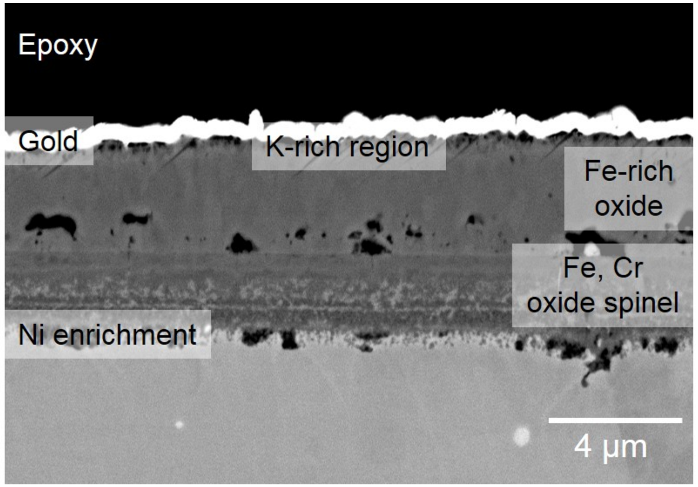


Folkeson, N., et al., *The influence of small amounts of KCl(s) on the high temperature corrosion of a Fe-2.25Cr-1Mo steel at 400 and 500 degrees C.* Materials and Corrosion-Werkstoffe Und Korrosion, 2011. **62**(7): p. 606-615.

Research strategy – Experimental plan



Influence of KCl and HCl: experimental starting conditions



Alloy	Fe	Cr	Ni	Mn	Si	C
347H	Bal	17.6	10.1	1.6	0.6	0.05

Oxidation time: 168 hours
Temperature: 600 ° C
Evironment: 5%O_2+N_2+1.35µmol K^+/cm^2 in form of K_2CO_3

Step 1: Pre-oxidation

Breakdown of protective oxide

$$\tfrac{1}{2}\,Cr_2O_3(s) + K_2CO_3(s) + \tfrac{3}{4}\,O_2(g) \leftrightarrow K_2CrO_4(s) + CO_2(g)$$

*Stability of the potassium chromate formed has earlier been reported to be low and after 168 hours it is seldom detected

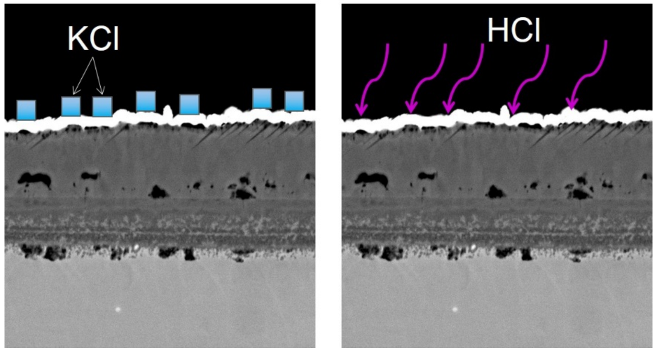
Formation of K-rich area

$$Fe_2O_3(s) + K_2CO_3(s) \leftrightarrow 2KFeO_2(s) + CO_2(g)$$

Influence of KCl and HCl: experimental starting conditions

Step 2: Exposure in presence of chlorine

Exposure time:
24 hrs
Temperature:

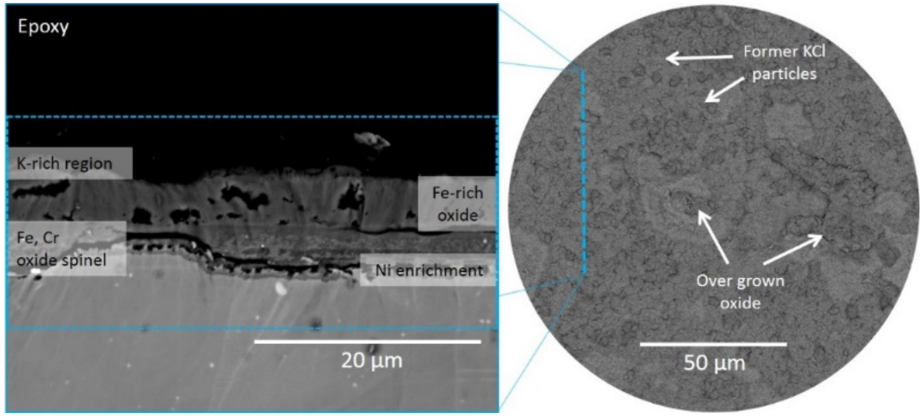


$5\%O_2+20\%H_2O+N_2$
$+$**$0.1mg/cm^2$ KCl**

$5\%O_2+20\%H_2O+$**500ppmHCl**$+N_2$

Influence of KCl and HCl: exposures in presence of Cl

Results: KCl(s)

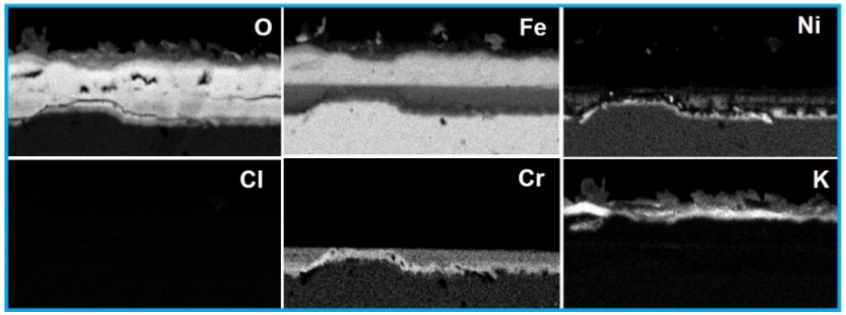


Oxide layers similar to pre-oxidation

No spallation

KCl evaporation

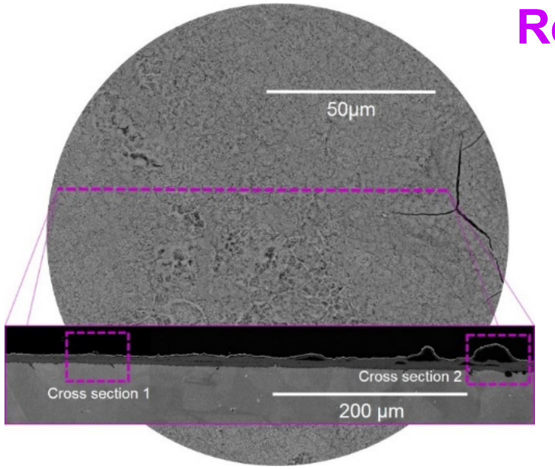
$KCl(s) \leftrightarrow KCl(g)$

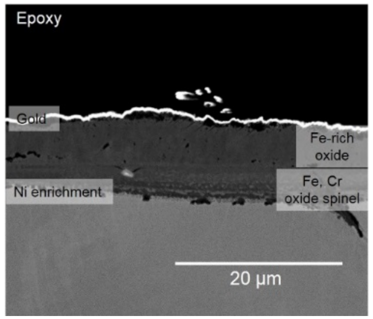


$Fe_2O_3(s) + K_2CO_3(s) \leftrightarrow KFeO_2(s) + CO_2(g)$

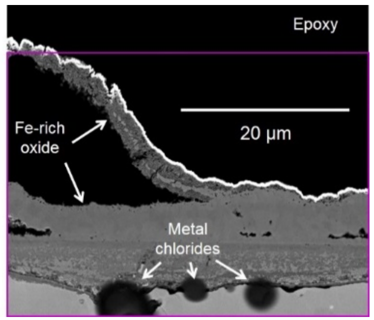
Influence of KCl and HCl: exposures in presence of Cl

Results: HCl(g)

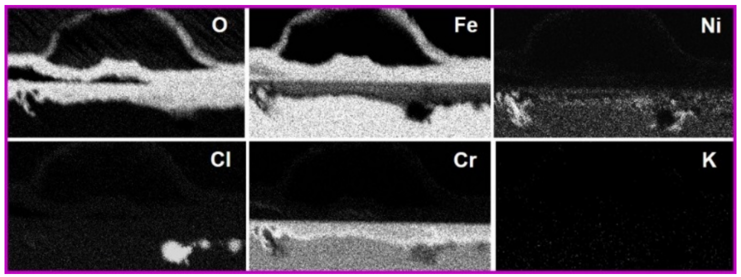




Cross section 1



Cross section 2



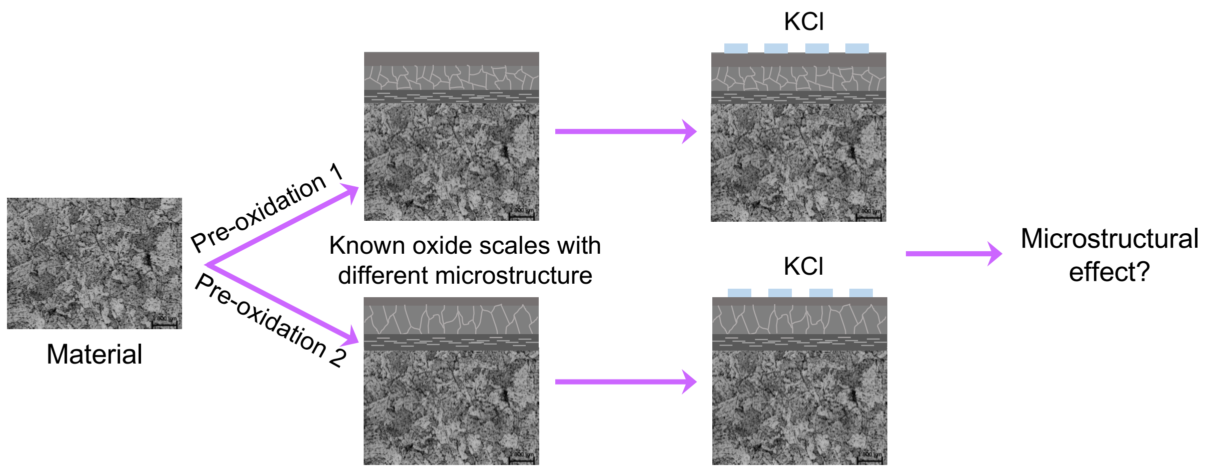
Presence of **chlorine** was detected at the oxide/metal interface beneath a region with blisters.

$$2HCl(g) + KFeO_2(s) \leftrightarrow Fe_2O_3(s) + KCl(s) + H_2O(g)$$

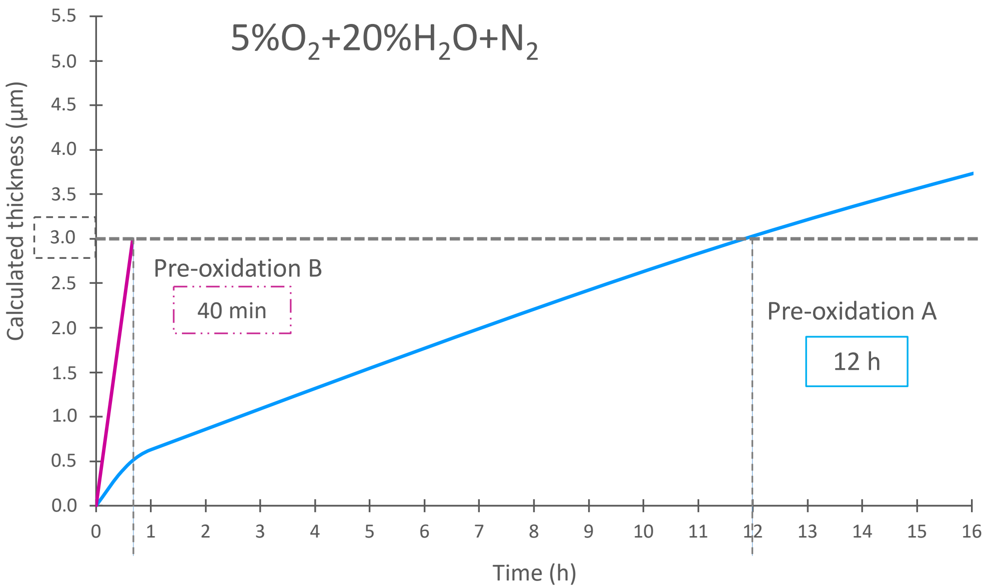
$$KCl(s) \leftrightarrow KCl(g)$$

*According to the XRD results, weak signals of iron and chromium chlorides were detected.

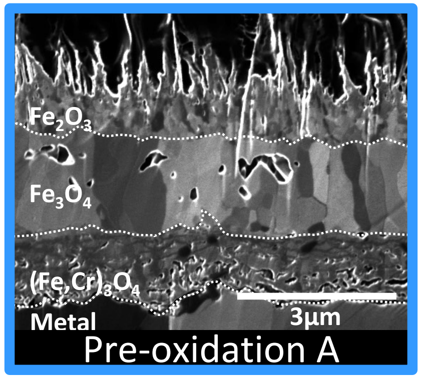
Research strategy – Experimental plan

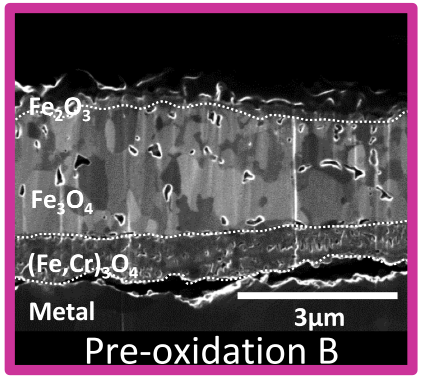


Pre-oxidation of low alloyed steel

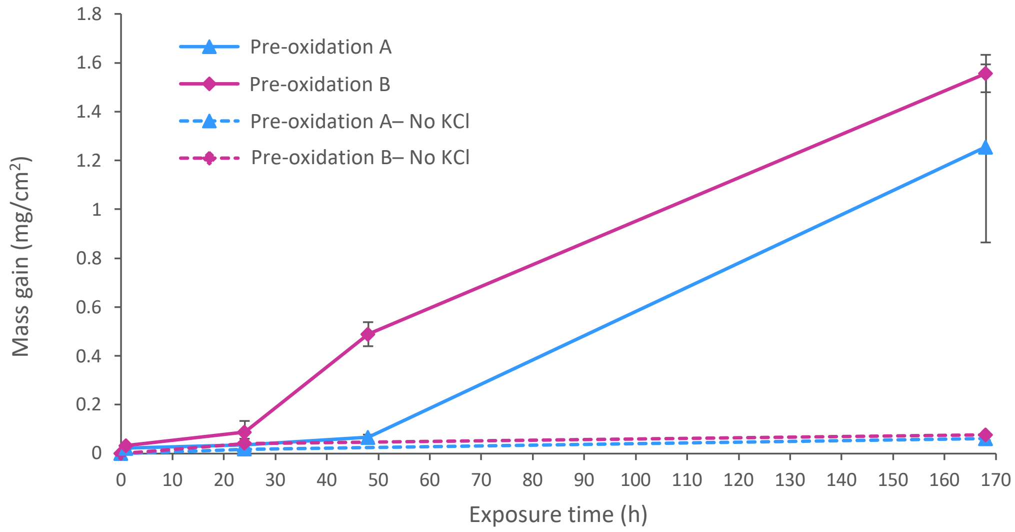


Material	Pre-oxidation name	Temperature
Fe-2.25Cr-1Mo	Pre-oxidation A	500 °C
	Pre-oxidation B	600 °C

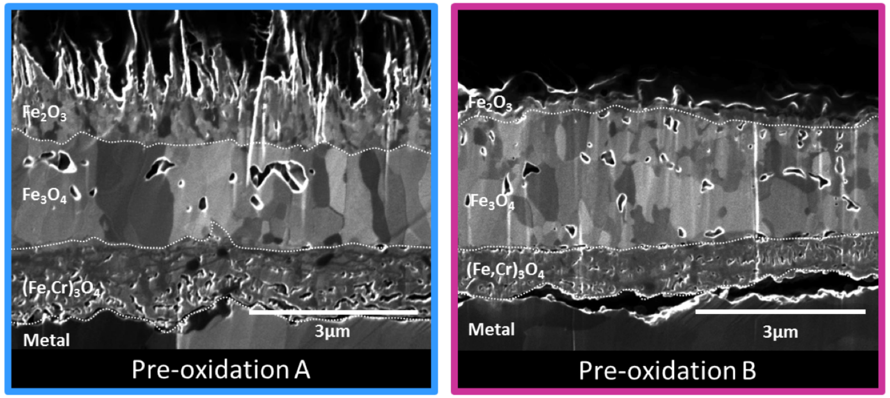




Chlorine-containing exposure – low alloyed steel



Atmosphere	Temperature (°C)	Time
5% O_2 + 20% H_2O + 75% N_2 + 0.1 mg/cm² KCl	400	1, 24, 48, 168 hours



Conclusions and Future Work

Laboratory exposures

→ Presence of KCl accelerates the corrosion rate on already oxidized samples.
→ There seems to be an effect of oxide microstructure on the propagation of corrosion attack. A difference in the incubation time to breakaway corrosion.
→ Longer exposure times are of great interest.
→ In KCl exposures, evaporization of KCl from the surface (no penetration of Cl). In HCl exposures, presence of chlorine was detected at the oxide/metal (no cracked oxide).
→ The transport of chlorine is suggested to occur by alternative diffusion paths different from cracks and pores.
→ More detailed microstructural study will be performed (TEM with EDS, EELS analysis).

Field exposures (KME711)

→ Study of propagation of corrosion attack in boiler environment in order to correlate lab results with actual situtation in the boiler.
→ There seems to be an initial effect of the preformed oxide in decreasing the inward diffusion of chlorine, even though the corrosion load is much higher.
→ The non pre-oxidized samples exhibited a slightly more accelerated corrosion attack and a thicker chlorine enriched corrosion product layer.
→ The corrosion attack was in general very fast.
→ Steel grain boundary attacks could be noted for both types of samples.

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The High Temperature Corrosion Centre

Influence of Constituents in FeCrAl Alloys on High Temperature Corrosion Resistance in Alkali-rich Environment

Johan Eklund, Amanda Persdotter, Sedigeh Bigdeli, Torbjörn Jonsson, Jesper Liske, Bo Jönsson, Jan Erik Svensson

KME 709, 711, 720

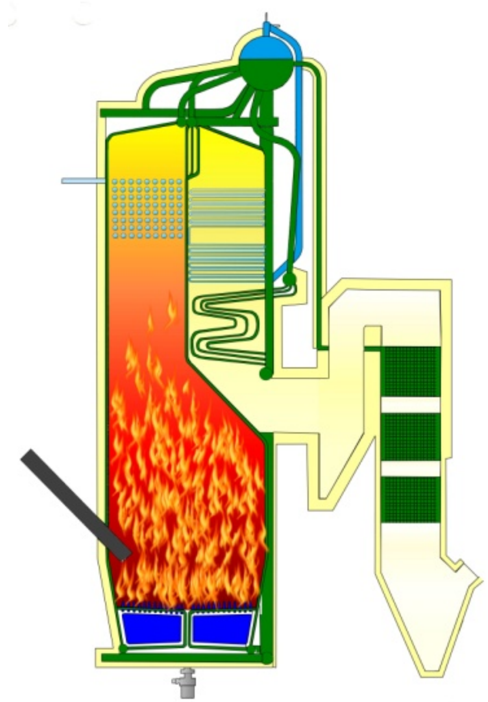
HTC1a - Critical Corrosion Phenomena

TEAMWORK

Background

- Renewable energy – Substitute fossil fuels
- Biomass and waste
  - Corrosive environment
    - Superheater
  - Higher steam temperature
    - Higher electrical efficiency

→ Need for more corrosion resistant materials



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The High Temperature Corrosion Centre

Our largest sponsor:

Energimyndigheten

The Swedish Energy Agency works for a sustainable energy system, combining ecological sustainability, competitiveness and security of supply.

Materials

Compound tubes

Low alloyed steels

Ferritic steels

FeCrAl alloys

Corrosion problems

Stainless steels

Nickel based alloys

Austenitic steels

Coatings

More than 3500 different steel grades exists today…

CONSORTIUM MATERIALS TECHNOLOGY

The High-Temperature Corrosion Center

Potential for using FeCrAl alloys in combustion environment

Why does FeCrAl alloys have potential?

- Highly stochiometric
- Low defect concentration
- Thermodynamically stable

- α-Al_2O_3 does not suffer from evaporation

- α-Al_2O_3 does not form chromates

Improved oxidation resistance

α-Al_2O_3
SiO_2
Cr_2O_3
α-Fe_2O_3

NiO
CoO
FeO

Challenges with FeCrAl alloys

Temperature

Applications

1400°C

1200°C

1000°C

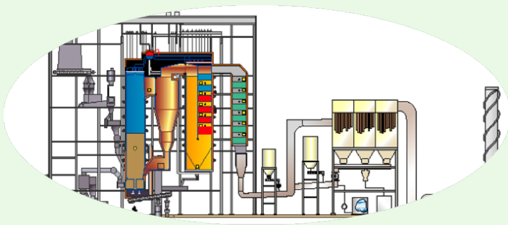
800°C

600°C

400°C

Heating elements

Boilers?

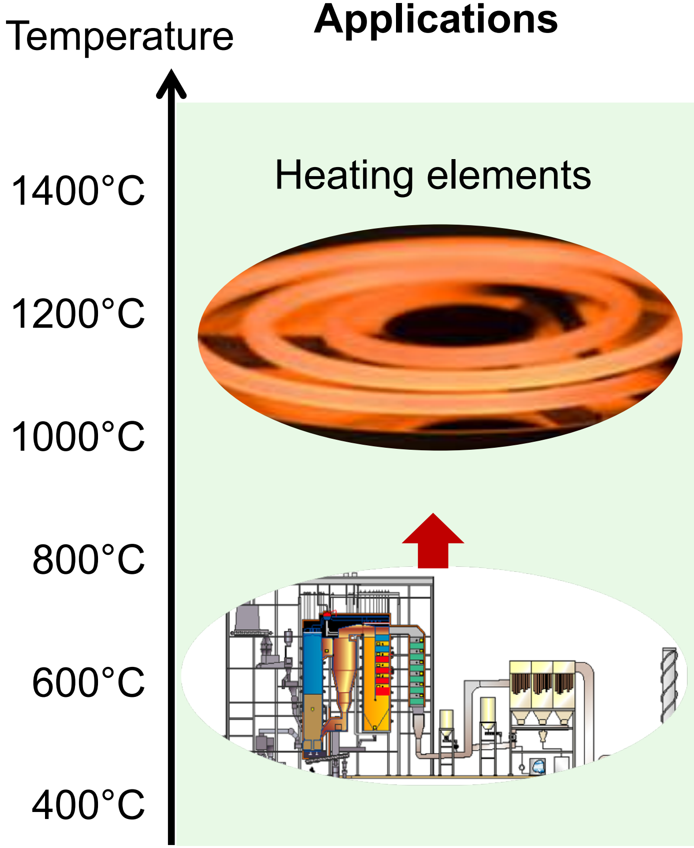


An α-alumina scale forms at temperatures above ~900 °C that protects the alloy

At lower Temperatures

- Metastable forms of alumina may form
- How protective are metastable alumina's?

Potential with FeCrAl alloys



An α-alumina scale forms at temperatures above ~900 °C that protects the alloy

- ❖ Replace steels in existing materials
- ❖ Higher boiler temperatures

FeCrAl alloys for combustion environments

FeCrAl alloys are potential materials for biomass and waste fired environments

Develop new FeCrAl alloys for biomass and waste fired environments

Existing FeCrAl alloys are optimized for higher temperatures

In close collaboration with Kanthal

Research direction
-FeCrAl

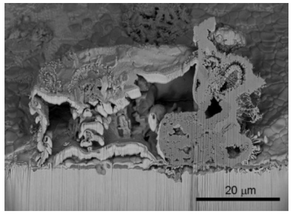
Model FeCrAl alloys – tailor made for biomass and waste fired boilers
- excellent oxidation resistance, good weldability and workability

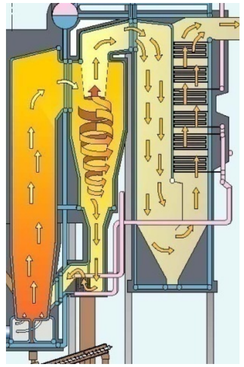
- Investigate effect of Cr content
  - ✓ For better weldability and less chromate formation
- Investigate effect of Al content
  - ✓ For better weldability, workability and corrosion resistance
- Investigate effect of other elements content
  - ✓ For increased corrosion resistance

Research strategy –
a two pronged approach

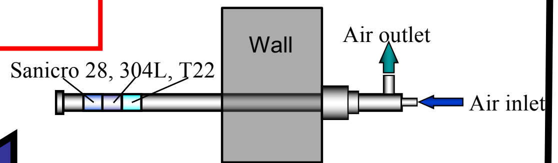
Fundamental research

Corrosion
mechanisms





Fundamental understanding of the corrosion process in boilers



Effects of
corrosion

Applied research

Laboratory
studies

Field
studies

Model alloys – Matrices

Alloy	Cr	Al	Other elements
1	5	3	Fe, Si, C, N, Zr
2	10	3	
3	15	3	
4	20	3	

Alloy	Cr	Al	Si	Other elements
1	10	4	0	Fe, C, N, Zr
2	10	4	1	
3	10	4	2	

- Contains reactive elements
- Contains Silicon

Research direction
-FeCrAl

Model FeCrAl alloys – tailor made for biomass and waste fired boilers
- excellent oxidation resistance, good weldability and workability

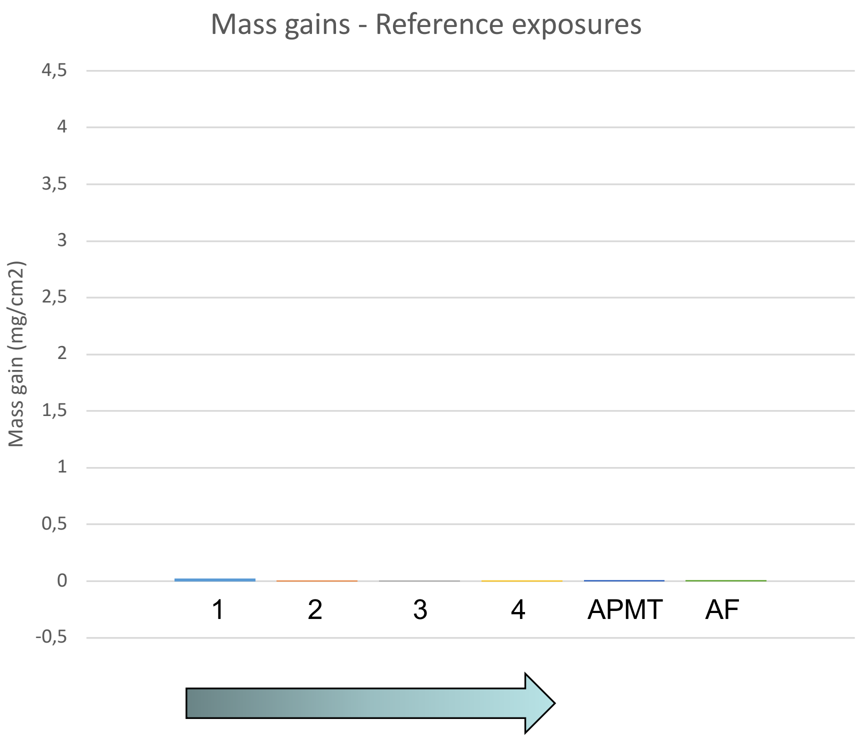
- Investigate effect of Cr content
  - ✓ For better weldability and less chromate formation
- Investigate effect of Al content
  - ✓ For better weldability, workability and corrosion resistance
- Investigate effect of other elements content
  - ✓ For increased corrosion resistance

Effect of Chromium – Exposure matrix

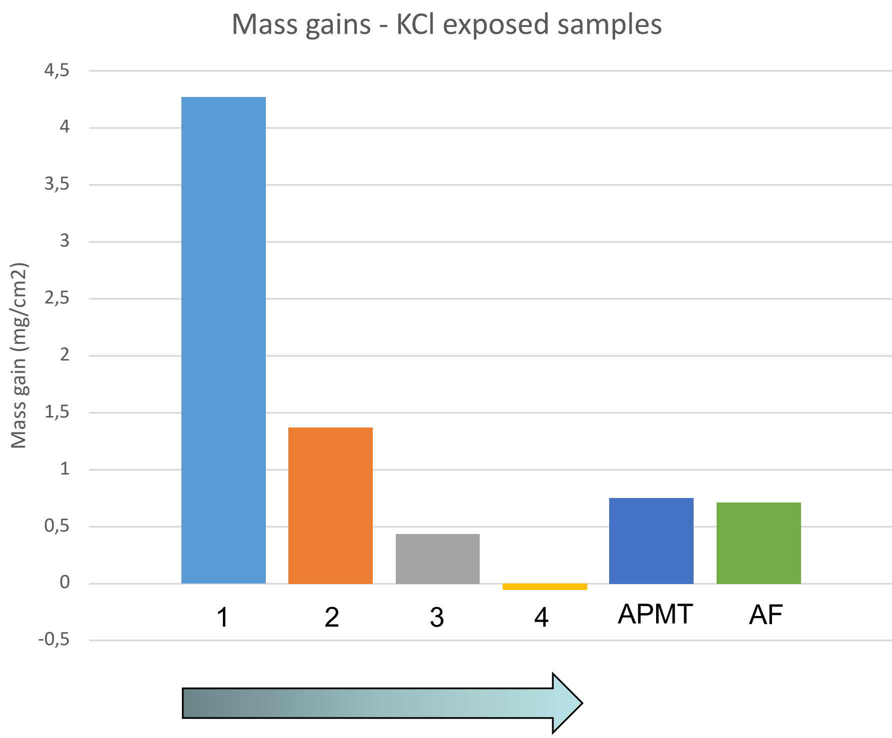
Alloy	Cr	Al	Other elements
1	5	3	Fe, Si, C, N, Zr
2	10	3	
3	15	3	
4	20	3	

Sample	Temperature (°C)	Time(h)	Environment
Reference	600	168	5% O_2 + 20% H_2O + 75% N_2
With KCl	600	168	5% O_2 + 20% H_2O + 75% N_2 +1.0 mg/cm^2 KCl

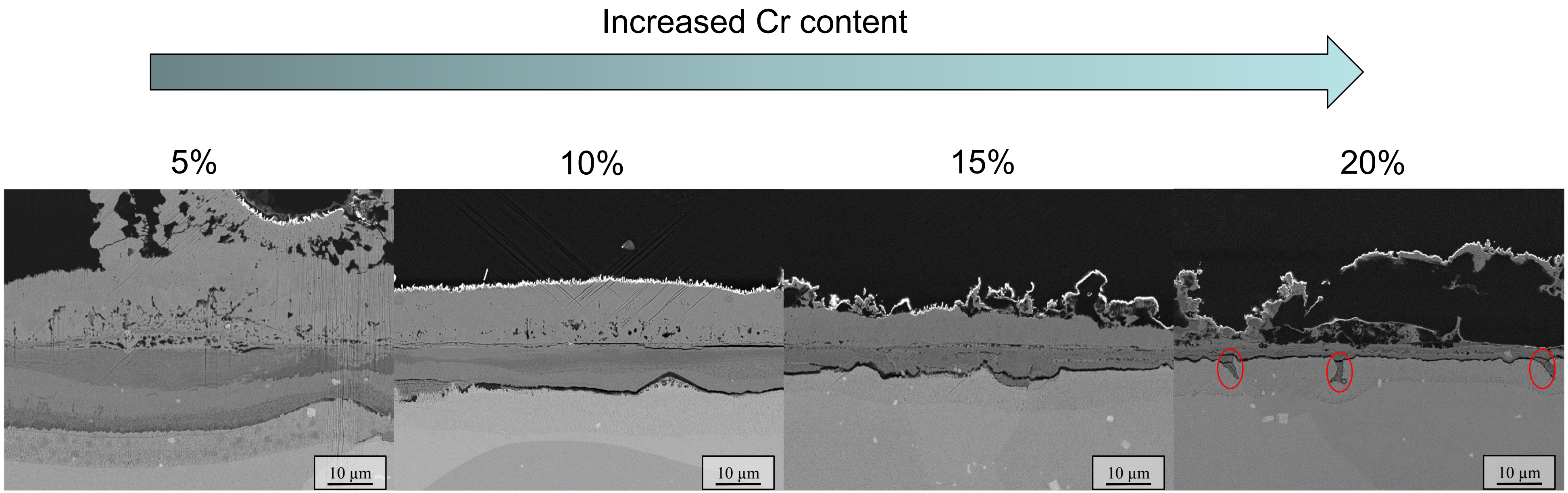
Mass gains after exposures



Increased Cr content



Increased Cr content



- Great beneficial effect of Cr on corrosion properties
  - Decreased oxide thickness

But:

- Increased formation of K_2CrO_4
- Grain boundary attack

Conclusions

- Great beneficial effect of Cr on corrosion resistance
  - Decrease in mass gain and oxide thickness

But:

- Increased formation of K_2CrO_4
- More prone to grain boundary attack

- Incubation time or better secondary protection → kinetic studies

Future work:

- Thermogravimetric in-situ exposures
  - Understand the kinetics
- More advanced microscopy (TEM)
  - Study the grain boundary attack
    - Initiation

Research direction
-FeCrAl

Model FeCrAl alloys – tailor made for biomass and waste fired boilers
- excellent oxidation resistance, good weldability and workability

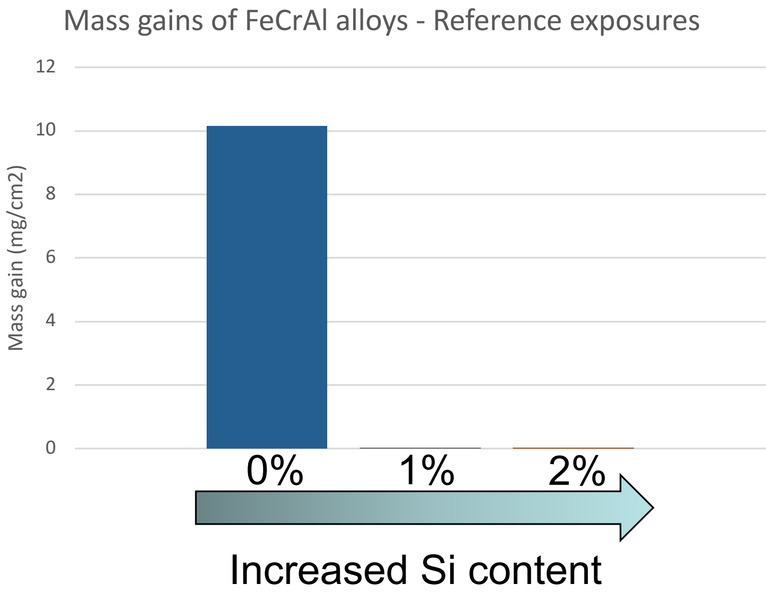
- Investigate effect of Cr content
  - ✓ For better weldability and less chromate formation
- Investigate effect of Al content
  - ✓ For better weldability, workability and corrosion resistance

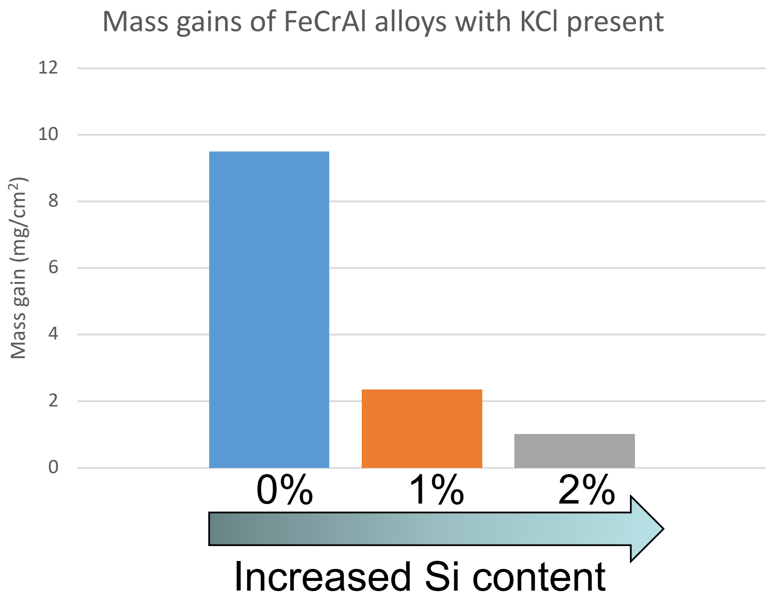
- Investigate effect of other elements content
  - ✓ For increased corrosion resistance

Effect of Silicon – Exposure Matrix

Alloy	Cr	Al	Si	Other elements
1	10	4	0	Fe, C, N, Zr
2	10	4	1	
3	10	4	2	

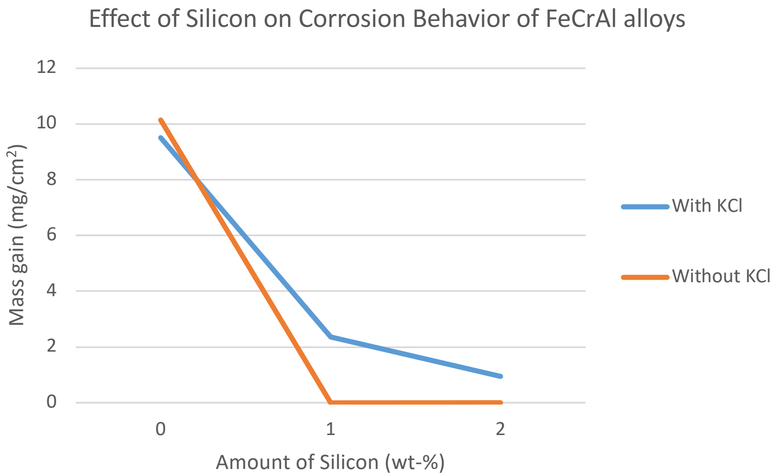
Sample	Temperature (°C)	Time(h)	Environment
Reference	600	168	5% O_2 + 20% H_2O + 75% N_2
With KCl	600	168	5% O_2 + 20% H_2O + 75% N_2 +1,0 mg/cm^2 KCl





Without KCl present:

- Large decrease in mass gain upon addition of Si
- Formation of protective oxide when adding Si

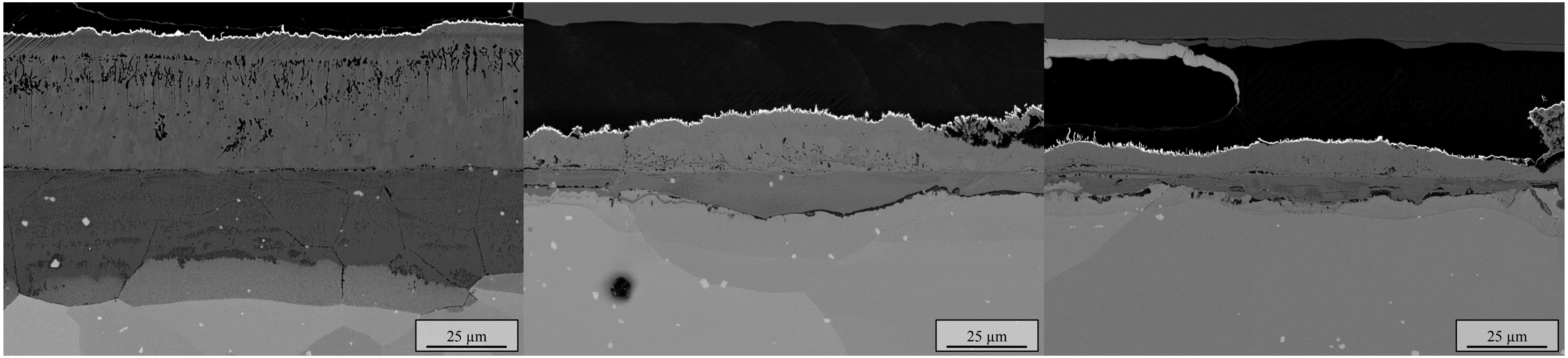


With KCl present:

- Large decrease in mass gain upon addition of Si
- Breakaway oxidation in all cases

Increased Si content

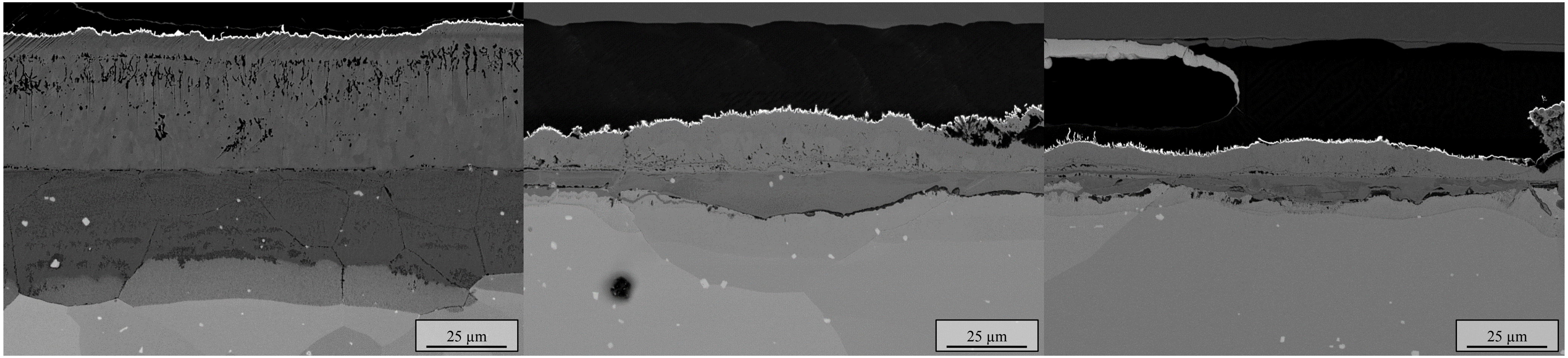
0% 1% 2%



- Observed oxide thickness correlates well with measured mass gains
    - Large decrease in oxide thickness upon addition of Si

Increased Si content

0% 1% 2%



- Observed oxide thickness correlates well with measured mass gains
  - Large decrease in oxide thickness upon addition of Si

However:

- No visible formation of SiO_2
- No significant accumulation of Si

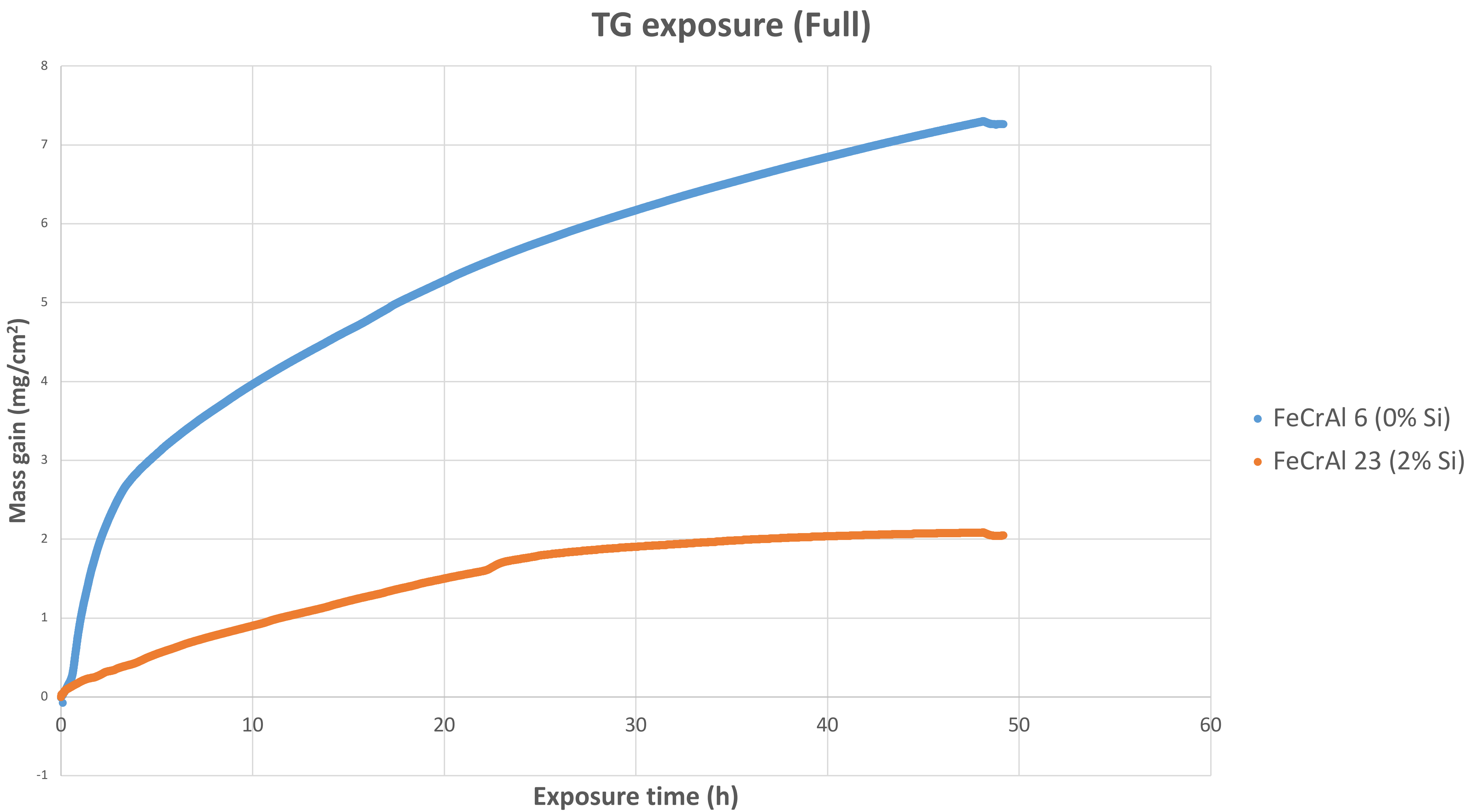
Very interesting effect

But:

The role of Si still not fully understood

Thermogravimetric in-situ exposures

- Study the initation of the corrosion attack
- Realize key events
- Subsequent microscope analysis



TG exposure (Full)
Mass gain (mg/cm²)
Exposure time (h)
8
7
6
5
4
3
2
1
0
-1
0
10
20
30
40
50
60
FeCrAl 6 (0% Si)
FeCrAl 23 (2% Si)

Conclusions

- Addition of Si shows **great beneficial effects** on corrosion resistance
  - Two different effects
    - Without KCl
      - Breaks without Si and retains thin oxide with Si
    - With KCl
      - Forms thick iron oxide in all cases but Si reduces the corrosion rate – Improved secondary protection

- The role of Si?
  - Formation of SiO_2 layer?
    - Not visible so far – TEM needed
  - Si changes the activity of Cr and/or Al? - Indicated by thermodynamic modelling
    - Refill chromia with Cr
    - More Al-rich oxide – less sensitive towards Cr-evaporation

Future work

- Further kinetic studies – Thermogravimetric in-situ exposures
  - Investigate effects of Cr and Al addition with and without Si-addition

- More advanced microscopy (TEM)
  - Investigate possibly formed SiO_2 layer
  - Analyze the composition of thin oxides with and without Si-addition

Thank you for your attention!